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Effect of Medium on the Formation Constants of Metal Complexes of Lactic Acid.

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EFFECT OF MEDIUM ON THE FORMATION CONSTANTS OF METAL COMPLEXES OF LACTIC ACID

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The author respectfully dedicate this volume to his dear departed mother, Francis Jane Hardy Gibbons, who instilled in him at an early age the benefits of obtaining a complete and thorough education.

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

a	radius of sphere to be charged
A^-	anion of the weak acid HA
a_i	activity of species i
C_A	concentration of free anion A^-
C_{HA}	concentration of weak acid HA
C_L	concentration of unbound ligand L
C_M	concentration of central metal atom (ion) M
C_{ML}	concentration of metal complex ML
C_i	concentration of species i in moles/liter
E_{corr}	E.M.F. of the hydrogen electrode - S.C.E. cell corrected to standard hydrogen pressure and standard hydrogen ion activity
E_{H_2}	potential of the hydrogen electrode
E_{meas}	measured E.M.F. of the hydrogen electrode-S.C.E. combination
E_j^m	liquid junction potential at the interface of the saturated aqueous potassium chloride solution and the mixed solvent test solution
E_j^w	liquid junction potential at the interface of the saturated aqueous potassium chloride solution and the aqueous test solution
$E_{S.C.E.}$	potential of the saturated Calomel electrode
$E_{H^+}(R)$	E.M.F. of the hydrogen electrode versus S.C.E. combination in aqueous medium with standard hydrogen ion solution at infinite dilution
$E_{H^+}(x)$	E.M.F. of the hydrogen electrode versus S.C.E. combination in mixed solvent system under investigation

ΔE	correction in the observed E.M.F.
e	electronic charge
f	function of (prefix)
F	Faraday's constant
GMWS	gram molecular weight of organic solvent
GMMW	gram molecular weight of water
ΔG	Gibbs free energy change
ΔG^{o}	standard Gibbs free energy change
ΔH	enthalpy change
ΔH^{o}	standard enthalpy change
$H^{+}_{(R)}$	A solution of known hydrogen activity
$H^{+}_{(x)}$	The unknown hydrogen ion activity in mixed solvent system
h	average depth of the jet of hydrogen in mm
HA	a weak monoprotic acid
HL	Lactic acid
K_a	ionization constant of HA
K_i	ionization constant of HL
K_{av}	average formation constant of metal complex in aqueous media
K^{*}_{av}	average formation constant of metal complex in mixed solvent media
K_{eq}	equilibrium constant
K_f	formation constant of ML
K_{ov}	overall (thermodynamic) stability constant
M	molar concentration, central metal atom (ion)
m_i	molality of species i
N	number of ligands bound to M, Avogadro's number
n	number of moles

$\bar{n}$	average number of ligands attached to central group
p	negative logarithm of (prefix)
pK_i	negative logarithm of K_i
pK_1	negative logarithm of K_1
pK_2	negative logarithm of K_2
pK_i^*	negative logarithm of K_i^*
pK_2^*	negative logarithm of K_2^*
pK_{av}	negative logarithm of K_{av}
pK_{av}^*	negative logarithm of K_{av}^*
P_{bar}	barometric pressure
P_{H_2}	corrected hydrogen pressure
P_w^0	vapor pressure of pure water
P_S^o	vapor pressure of pure organic solvent
P_w	partial pressure of water in the mixed solvent system
P_S	partial pressure of organic solvent in the mixed solvent system
$pH_{(R)}$	pH of a solution of known hydrogen activity
$pH_{(x)}$	pH of a solution of unknown hydrogen activity in mixed solvent system
q	electrical charge
r_i	mean ionic radius of sphere to be charged
r_+	mean ionic radius of cation
r_-	mean ionic radius of anion
R	Ideal Gas Law constant
ΔS	entropy change during chelation
ΔS^o	standard entropy change during chelation
S.C.E.	saturated Calomel electrode

S	subscript denotes measurement (or quantity) relative to infinite dilution in mixed solvent, total concentration of dissociated and undissociated ligand
T	absolute temperature
t	temperature, degrees Celsius
TC_{HA}	total concentration of weak acid HA
TC_M	total concentration of central metal ion M
TNM	total number of moles in the mixed solvent system
TNMS	total number of moles of organic solvent in the mixed solvent system
TNMW	total number of moles of water in the mixed solvent system
v_+	number of positive ions produced per molecule by molecular dissociation
v_-	number of negative ions produced per molecule by molecular dissociation
W	work involved in charging an ion
W_{total}	total work necessary to charge an ion in a given complex in one solvent with respect to the work necessary in another solvent
W_+	work necessary to charge a given cation
W_-	work necessary to charge a given anion
XS	mole fraction of organic solvent in mixed solvent media
XW	mole fraction of water in mixed solvent media
x	Bjerrum's spreading factor
X	concentration of organic solvent in mixed solvent media being measured by experimental cell

Y	concentration of water in mixed solvent media being tested in experimental cell
z_+	charge on cation
z_-	charge on anion
β	proportionality constant from Born equation
β_n	product of individual formation constants for first n steps
$\gamma_{\pm}$	mean activity coefficient
γ	slope of the formation curve
δ	slope at the midpoint of the degree of formation curve
μ	ionic strength
ϵ	dielectric constant of water
ϵ^*	bulk dielectric constant of the mixed solvent media
$\epsilon^{*'}$	$\epsilon + (\epsilon - \epsilon_{organic})$
$\epsilon^{*''}$	$\epsilon^* + (\epsilon_{MeOH} - \epsilon_{organic})$
ϵ''	$2\epsilon - \epsilon_{organic}$
$\epsilon^{*''}$	$\epsilon^* + (\epsilon - \epsilon_{organic})$
*	measurement made in mixed solvent

ABSTRACT

This dissertation reports the results of a part of a program of research which has, as one of its objectives, the determination of an analytical function for transforming the thermodynamic values of a reversible process computed from experimental data obtained in one solvent system to the corresponding thermodynamic values for the same reversible process in other solvent systems.

Previous work by Sen, Roy, Johnson and Adcock, indicated that the system $M^{2+} + n\ CH_3CH(OH)CO_2H \rightleftharpoons M(CH_3CH(OH)CO_2)_n^{2-n} + n\ H^+$ might be suitable for such a study. The foregoing equilibrium and the ionization equilibrium of lactic acid were studied in three different mixed solvent systems at seventeen different compositions altogether, and at four different temperatures. The mixed solvent systems used were methanol-water, ethanol-water, and glucose-water.

It has been found that the average formation constant K^*_{av} of ML_2 (M = Ca(II), Zn(II), and Fe(III); L = $CH_3CH(OH)CO_2^-$) at zero ionic strength in any one of the mixed solvents mentioned above, and the average formation constant K_{av} of ML_2 at zero ionic strength in water, may be related by the equation

$$\log K^*_{av} = \log K_{av} + (1/\epsilon^{*''} - 1/\epsilon'')$$

in which $\epsilon^{*''}$ and ϵ'' are certain linear combinations of the buld dielectric constants of the mixed solvent, water and the organic component. Plots of K^*_{av} versus $(1/\epsilon^{*''} - 1/\epsilon'')$ deviate from linearity in the segment of the plot which corresponds to a very low bulk dielectric constant of the solvent, and consequently the correlation equation requires an additional exponential term to meet this situation.

The foregoing equation is quite analogous to the equation derived by Sen and Adcock to correlate data determined for thirteen monocarboxylic acids in six different solvents.

It has been speculated from the magnitude of the successive formation constants (K_1, K_2) that two lactate ions are attached to each metal ion. Attachment of the enolic groups to the Ca^{2+} and Zn^{2+} ions is endothermic, and so is the overall process. Therefore, it has been concluded that the formation of calcium lactate and zinc lactate and zinc lactate in solution is entropy driven.

CHAPTER I

INTRODUCTION

In discussing coordination chemistry, it is necessary that a common understanding of the general terms employed be reached; hence, certain definitions are in order to help establish a fundamental background of the subject before proceeding into more elaborate theory.

The central atom is the atom which accepts the electron pair to form the coordinate-covalent bond. In this dissertation, the term central metal atom or ion will simply refer to either the Ca^{2+}, Zn^{2+}, or Fe^{3+} ion.

The ligand, also called the coordinating group, is that neutral molecule or charged species which contributes the electron pair or pairs to the central atom to form the coordinate-covalent bond. A donor group is classified as a monodentate (Greek, "one-toothed"), bidentate (Greek, "two-toothed"), or a tridentate (Greek, "three-toothed"), etc., ligand, depending upon the ability of the donor group to coordinate via one, two, or three, etc., atoms to the central metal atom (ion), and thus form one, two, or three, etc., coordinate-covalent bonds, respectively.

Ligands with two or more appropriately situated electron pairs that can act as donating groups, and which may thus coordinate through more than one position, are referred to collectively as polydentate groups. Polydentate ligands whose structures permit the attachment of two or more donor sites to the same central metal atom (ion), thus closing one or more rings, with each ring containing the metal atom (ion), are called chelating (from the Greek word for "claw") ligands. The compound that is formed when a metal ion combines with a chelating ligand is called

a chelate compound.

THEORIES OF MODERN COORDINATION CHEMISTRY

In the recent past, several theories have been expounded in an effort to explain the formation, stability, spectral, magnetic, and other physico-chemical properties of coordination compounds. A brief qualitative summary of each of these theories is presented in the following paragraphs.

Valence Bond Theory. Electron-pair Valence Bond (VB) theory in its simplest form was originally postulated by Lewis (68). This theory was subsequently given semi-empirical quantum mechanical interpretation by Heitler and London (54), Slater (96), and Pauling (22). Pauling greatly enlarged the scope of application of the VB theory, and he was particularly successful in interpreting the structure of coordination complexes with the help of some additional postulates. The essential postulates of the VB theory as applied to coordination complexes are:

(1) The central metal atom must make available a number of stable orbitals equal to its coordination number for the formation of covalent bonds with the suitable ligand orbitals. Only stable ligand orbitals enter into covalent bonding, and the strongest covalent bonds arise from the greatest amount of overlap between the ligand orbitals and the central metal orbitals. The ligand orbitals are not specified precisely by this model, but are assumed to be filled σ-bonding orbitals.

(2) The donor group or ligand must therefore be a chemical species which contains at least one lone pair of electrons. The resulting coordinate bond is seen to be simply a covalent bond between the central

atom (ion) and the donor atom, involving the characteristic overlap of two directed orbitals, one from each of the bonded atoms. The strongest covalent bond will be formed when the charge clouds overlap one another as much as possible. In order to satisfy this criterion, it has been shown (22) that generally the set of original atomic orbitals should be hybridized to form a new set of equivalent bonding orbitals which possess definite directional properties. It should be pointed out that hybridization may not always produce a set of equivalent orbitals.

(3) A covalent σ bond arises from the overlap of a vacant metal orbital and a filled σ orbital from the donor group. The metal orbital may be a hybrid orbital formed by a suitable combination of the available s, p, and d orbitals

(4) In addition to the σ bond, there is also allowed in later Valence Bond treatments (14) the possibility that a π bond may form, providing that suitable d orbitals and electrons are present on the metal atom and that overlap with ligand π orbitals can occur. This kind of bond, if it is (M--L)π, will alter the charge distribution in such a way as to strengthen the σ bond. If it should be (L--M) π bonding (usually not considered in the earlier Valence Bond treatments) the σ bond might be weakened, but the overall bond strength would be increased.

Crystal Field Theory. The forerunner of the Crystal Field theory, a simple electrostatic approach, is based on classical electrostatics (49, 106). A potential energy equation can be derived from the charge and the size of the metal ion, and from the charge, size, dipole moment, and polarizability of the ligand (101). All bonding is thus described as purely electrostatic in nature and all configurations are expected

to be linear, trigonal, tetrahedral, octahedral, etc., provided that the ligands approach the metal in such a manner as to minimize ligand-ligand repulsion. Although this simple model is able to give reasonable bond energies in some instances, it is unable to account for many other physically observable properties (e.g., magnetic and spectral properties) and also cannot account for the -bonding of complexes.

The Crystal Field Theory (21), in spite of its conceptual simplicity and mathematical elegance, is not a bonding theory in a strictly chemical sense. The conceptual ideas of this theory were expounded as early as 1929 by Bethe (36). After a lapse of nearly a decade, this theory was revived, modified and expanded by Van Vleck (107, 108, 109), Sugano and Tanabe (98, 99, 100), Orgel (77, 78, 79, 80), Longuet-Higgins (71), Racah (85, 86, 87), etc. The theory in its oversimplified presentation considers a coordination compound as a central point charge (the central metal atom) surrounded by an ordered array of point charges (the ligands). The surrounding point charges are supposed to represent the donor atoms or the donor groups of the ligands; the central metal atom and ligands are held together in the array by electrostatic forces. Under the influence of the electrostatic field (the crystal field) of the surrounding ligands (depicted as point charges), the degeneracy of the metal d-orbitals of the free atoms of the transition metal series is removed. Occupancy of the d-orbitals is therefore dictated by the relative energies of the d-orbitals and Hund's first rule as a first approximation.

Let us consider a d^4 metal ion in an octahedral array of ligands. It can be shown (13) that the five-fold degeneracy of the d-orbitals is removed in this field; three of the d-orbitals (d_{xy}, d_{xz}, and d_{yz}) are lowered in energy and are labelled as t_{2g} (a symmetry notation), while

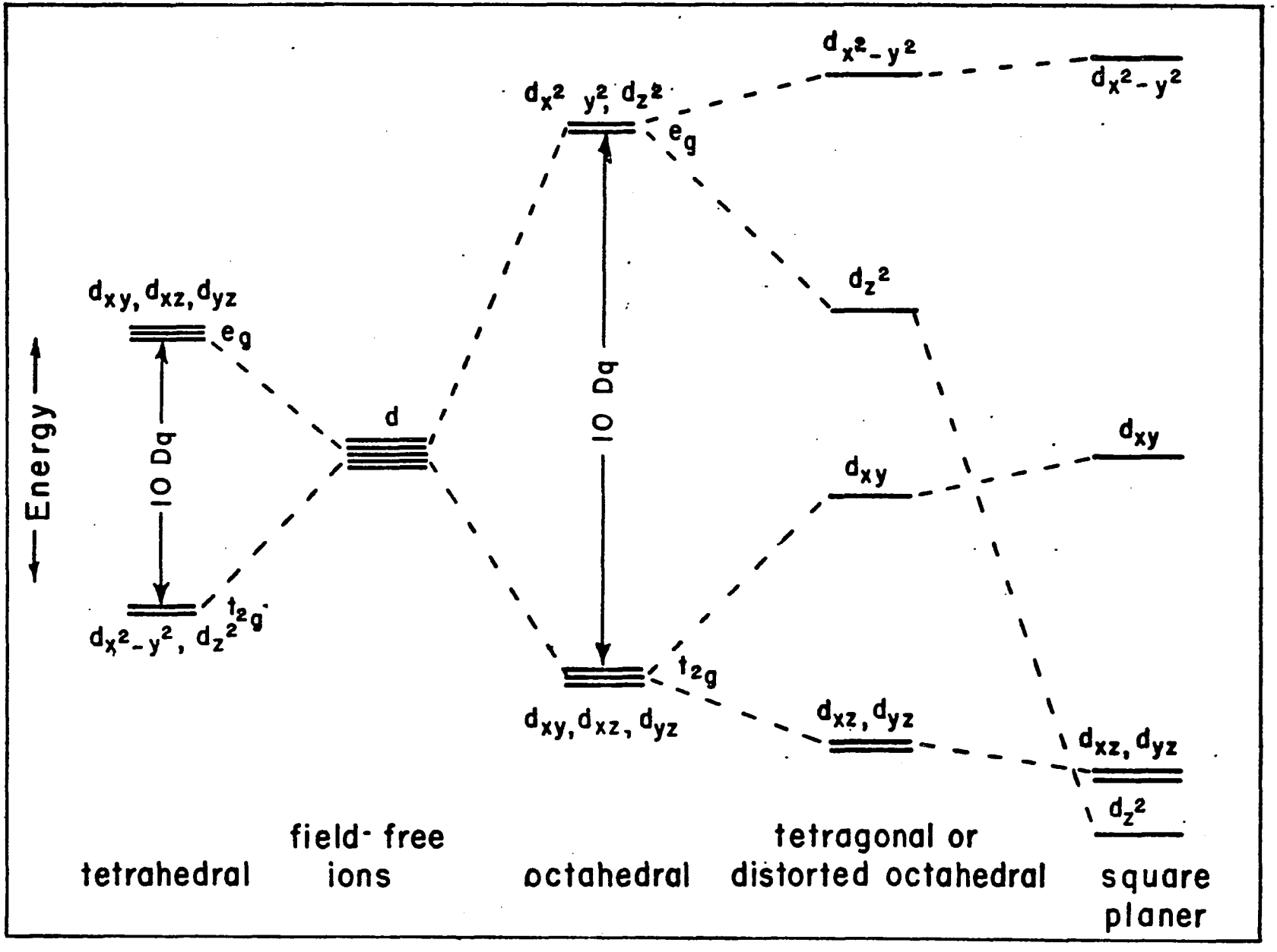
two of the d-orbitals ($d_{x^2-y^2}$ and d_{z^2}) are raised in energy and are labelled e_g (a symmetry notation). Instead of a five-fold degeneracy, we now have a triply degenerate t_{2g} set of orbitals and a doubly degenerate e_g set of orbitals. The energy difference, called the Crystal Field Stabilization Energy (C.F.S.E.) between the lower t_{2g} set and the higher e_g set is such that the center of gravity (or baricenter) of the energy of the t_{2g} and e_g sets is the same as the energy of the five unperturbed d-orbitals.

There is no problem in placing the first three d-electrons (cf. Figure 1); the energy level (either t_{2g} or e_g) to which the fourth d-electron will go is determined by two opposing factors--the C.F.S.E., and the pairing energy. If the C.F.S.E. is greater than the energy required to pair two electrons within the same d-orbital, the fourth d-electron will go to the t_{2g} level, giving rise to a so-called "low spin" complex. In this situation, the C.F.S.E. must be large enough to overcome the destabilizing effects of coulombic repulsion as well as the unfavorable exchange energy. On the other hand, if the C.F.S.E. is less than the pairing energy, the fourth d-electron will go into one of the e_g orbitals, retaining the maximum spin multiplicity and giving rise to a so-called "high spin" complex.

The overall symmetry of the array of metal ion and surrounding donor groups (ligands), which is the symmetry of the coordination complex itself, determines the splitting pattern of these energy levels. Such an energy level diagram is shown in Figure 1 for complexes possessing different symmetries. Electronic transitions are now possible between any of these energy levels, even between two d-orbitals which may be forbidden due to symmetry considerations (Laporte forbidden) (67).

FIGURE 1:

ENERGY LEVEL DIAGRAM SHOWING d-ORBITAL SPLITTING FOR COMPLEXES OF SEVERAL DIFFERENT SYMMETRIES


Energy
10 Dq
d_{xy}, d_{xz}, d_{yz}
e_g
t_{2g}
$d_{x^2-y^2}, d_{z^2}$
d
10 Dq
$d_{x^2-y^2}, d_{z^2}$
e_g
t_{2g}
d_{xy}, d_{xz}, d_{yz}
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz}, d_{yz}
d_{xy}
d_{xz}, d_{yz}
d_{z^2}
tetrahedral
field-free ions
octahedral
tetragonal or distorted octahedral
square planer

This is one of the successes of the Crystal Field theory, in that it allows for certain d-d transitions which, although forbidden by the Laporte selection rule (67), are nonetheless experimentally observed. These transitions are responsible for the absorption spectra of certain metal complexes in and near the visible region.

The Crystal Field theory has recently gained considerable recognition, not only because of its success in predicting stereochemistry and magnetic properties, but also in its wide application to kinetics, exchange mechanisms, and the absorption spectra. In fact, with modern modifications, the Crystal Field theory can be used to predict the electronic spectra in the region of 10,000 cm^{-1} to 30,000 cm^{-1}, in addition to explaining certain other phenomena, such as the order of the heats of hydration for certain metal complexes, their relative sequence of ΔG^{o} values, etc. However, the CFT has failed to rationalize the spectra of the complexes of the metals of the second transition series and the complexes of the lanthanides.

Ligand Field Theory. Whereas the term Crystal Field theory (CFT) generally refers to a purely electrostatic interaction between ligands and the central metal ion (i.e., covalency is excluded), it is possible to modify the theory to include some covalency. This modification is usually called the Ligand Field theory (2).

The Ligand Field theory differs from the Crystal Field theory in its first two basic assumptions:

(1) the ligands are envisioned as being point dipoles (rather than point charges as they were in the CFT).

(2) there is allowed a certain amount of mixing between the metal

ion d-orbitals and the incoming ligand orbitals (or, in other words, the metal d-orbitals may now assume a partial ligand orbital character).

The theory, then, is primarily an extension of the CFT, one that incorporates the best features of both the Valence Bond theory picture of pure covalency in coordination complexes and the Crystal Field theory model, with its concern for principally electrostatic interactions between the central metal ion and the surrounding donor groups or ligands. This modification also relieves the Laporte forbiddenness of the d-d transitions and allows them to gain intensity.

Molecular Orbital Theory. This theory, which resulted from the contributions made by Wolfsberg and Helmholtz (111, 112), Mulliken (75, 76), Huckel (55), and others, assumes the formation of a set of molecular orbitals from the linear combinations of the appropriate atomic orbitals of the atoms in the molecule. The nature of these linear combinations for the formation of the molecular orbitals is determined by the symmetry of the molecule. As a first approximation, these symmetry correct M.O.'s (wavefunctions) are used as the solutions of the molecular Schrodinger wave equation. However, the foregoing simple (perhaps even naive) description of the M.O. theory totally belies the tremendous mathematical complexity of the M.O. theory. In fact, a comprehensive understanding of the M.O. theory is not possible without going through the mathematical rigors. Therefore, only a simple listing of the salient features of the M.O. theory is presented here, to include its pertinent assumptions, operations and conclusions.

The M.O. theory is conceptually more realistic than either the VB theory or the CFT and its various modifications (LFT). Both of these

theories may be treated as special or partial solutions of the M.O. theory. In constructing the symmetry correct M.O.'s, only the valence shell atomic orbitals (A.O.'s) are considered; the closed shells are assumed to be unperturbed by bond formation, so that their only effect is to screen the atomic nuclear charge. The M.O.'s are stabilized by the resultant multicenter nucleus. The molecular electronic configuration is then built up according to the Aufbau principle (German: to build upon) with due consideration to Hund's rules and Pauli's exclusion principle.

The operational procedure is as follows: First, the valence A.O.'s of the combining atoms are classified according to the point group symmetry of the molecule. This classification requires application of symmetry operators (group theoretical techniques) (6). The A.O.'s with identical symmetries are then combined and normalized. Each such linear combination of atomic orbitals that forms a molecular orbital (LCAO-MO) is then given a symmetry label, such as a_{1g}, e_g, t_{1u}, t_{2g}, etc., which is simply the information regarding new coordinates of the angular portion of the wavefunction that results from the application of the various symmetry operators to the molecule. The next step (6) is to solve a set of secular determinants of the form

$$\begin{vmatrix} H_{ii} - E & H_{ij} - ES_{ij} \\ H_{ji} - ES_{ji} & H_{jj} - E \end{vmatrix} = 0$$

where H_{ii} is an integral of the form

$$H_{ii} = \int \varphi_i \, \mathcal{H} \, \varphi_i \, d\tau$$

that gives the energy of the atomic orbital φ_i; H_{ij}, and H_{ji} are exchange integrals of the form

$$H_{ij} = \int \varphi_i \, \mathcal{H} \, \varphi_j \, d\tau \quad \text{and} \quad H_{ji} = \int \varphi_j \quad \varphi_i \, d\tau$$

which give the energies of interaction between pairs of atomic orbitals; S_{ij} and S_{ji} are overlap integrals of the form

$$S_{ij} = \int \varphi_i \, \varphi_j \, d\tau, \text{ which equals } S_{ji} = \int \varphi_j \, \varphi_i \, d\tau$$

which represent the amount of overlap between the charge clouds of the atomic orbitals; and E is the energy of the system as determined by the Hamiltonian operator $\mathcal{H}$. The numerical values of the H_{ii}'s and H_{ij}'s and S_{ij}'s (which are also equivalent to the S_{ji}'s) can be approximated, estimated or computed to some level of accuracy, and the secular determinant can then be solved for the values of E. These computations could, until recently, only be performed for the simpler molecules, but with the advent of large computers, M.O. computations are being performed on larger and more complex molecules.

Successes of the MO theory have been numerous. This theory has been applied by Lipscomb (70) in his MO treatment of only one part of a molecule (the larger boron hydrides) with great success. It has also been the only theory of bonding that can adequately describe the two-electron, three-center bonds which occur in such molecules. The MO theory has been used in the treatment of an electron pair bond (7), and accounts for such bond formation with as much credence as the VB theory. The MO theory has been successfully applied to a certain segregated part of a molecule by Huckel (55), in his examination of the electron aromatic systems. He was the first to show the utility of the MO theory in its application to a single class of orbitals which may be found in a wide variety of seemingly unrelated molecules. Hence, it can be seen that its implications in describing bond formation in a large number of coordination compounds is promising. This listing will remain incomplete if the success of the MO theory in describing the formation and

stability and the spectra of inorganic -complexes (the so-called sandwich compounds) is not mentioned.

STABILITY OF THE CHELATES

One of the most important properties of any chemical entity is its ground state energy, which can only be provided by spectroscopic data, which, in turn, will require an interpretation in terms of an energy level diagram. We have seen that the prospects along that line are not yet very promising, except in the simplest cases.

However, in chemical studies, we are frequently more concerned with relative stabilities, because a vast majority of chemical reactions are carried out in solvent media. The methods of thermodynamics provide excellent avenues for such studies, because the laws of thermodynamics are independent of any atomic or molecular model.

It should be realized that the formation constants of complexes concern and relate to reactions between different solvated reactants and products. They are dynamic properties of solvated species existing and reacting in solution.

Once such formation constants are precisely computed, under favorable mathematical conditions, these values may be utilized to yield the thermodynamic functions of chelates and the process of chelation with respect to a reference state which we can set arbitrarily. However, from a more practical standpoint, one experiences many difficulties in the attempted application of the theory, as the method is fraught with many problems. (In fact, it is doubtful whether absolute thermodynamic quantities of chelation can be obtained from studies in solution.)

Two principal procedures are followed in studying the formation or stability constants of the chelates. Lewis and Randall (18) were the first to introduce the concept of ionic strength, which later received theoretical justification from the Debye-Huckel theory (20). The classical approach to the evaluation of thermodynamic equilibrium constants involves the experimental determination of the equilibrium constants in media of different ionic strengths, followed by an extrapolation to zero ionic strength (the case of infinite dilution). For water soluble chelates, this probably is the easiest and best method. Izatt, et.al.(57), have used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant through the application of the Debye-Huckel theory. A second approach was introduced by Biedermann and Sillen (37) and has been used extensively by them and the Swedish workers. The fundamental idea behind this method is to control the activity coefficient by maintaining a constant ionic strength, because of the fact that in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength (12). Rossetti and Rossetti (24) concluded that it would seem better to obtain reliable values of the stoichiometric constants (which describe the stability constants of a species relative to the corresponding complexes with solvent molecules and ions within the system) than to determine less certain values of the thermodynamic constants (which do not give a measure of the absolute ionic stability, either, but only stability relative to the solvated species).

When the chelates are insoluble in aqueous media, they are quite frequently studied in water-organic mixed solvent systems. Calvin and

Wilson (41) were the first to use a dioxane-water system to study chelate stability. Since then, numerous workers have used mixed solvent systems to study the thermodynamics of chelation. Sen and Al-Komser (94) and Shuman and Sen (95) studied the thermodynamics of chelation of metal ions with - furfuraldoxime and phenyl-2-pyrridylketoxime with reference to zero ionic strength in dioxane-water systems.

This, of course, immediately raises the question, "what is the reference state?". There are numerous advantages in accepting the infinitely dilute solution of the reaction system in aqueous media as the reference state. Therefore, appropriate corrections must be made for what are known as the primary and secondary medium effects. The most important is the primary medium effect. The explicit thermodynamic expression for the primary medium effect has been derived by Owen (81) and by Irving and Rossetti (56). In essence, the primary medium effect is the partial molal free energy of transfer of the solute species at infinite dilution from one solvent to another (12).

This dissertation is part of a continuing program to determine an analytical function for converting thermodynamic values computed from experimental data obtained for a reversible process in one solvent to the corresponding values in another solvent -- such as water. In the past, other authors have examined certain aspects of the study that should be considered as segments in a long range investigation dealing with the physical and thermodynamic properties of metal chelates and related compounds (such as the ionization constants of organic acids which may behave as ligands in these metal complexes). Roy and Sen (88), for example, proposed and verified with a polynomial curve-fitting technique an extension of the Debye-Huckel limiting law (43) along the

lines suggested by Grenwall, LaMer and Sandved (51), which related the standard electrode potential of HCl in several mixed solvent systems to a power series in $m^{1/2}$, where m is the molality of the acid. Sen and Adcock (93) derived a relation between the bulk dielectric constant of the mixed solvent media being studied and the ionization constants (in the form of $_pK_i^*$'s) of a series of monoprotic organic acids which may also act as ligands.

Various Methods of Studying the Stability of Chelates

(1) pH Measurements

If the precursor of the ligand is a protic acid, then chelation will result in a decrease in the pH of the entire system. Therefore, if the chelate thus produced and the reacting species are both soluble in aqueous or a suitably chosen mixed solvent medium, then the process of chelation can be followed by monitoring the pH change of the reaction system by potentiometric means. This approach was initially advocated by Bjerrum (4) and since then has become one of the most commonly used and dependable methods for the determination of coordination complex formation constants. This method will be discussed in more detail later when the theoretical treatment of Bjerrum's method is considered in the section devoted to theory.

(2) Ion Exchange

Both cation and anion exchangers have been used to study the formation constants of complexes in solution, but cation exchangers appear to be more commonly used for the quantitative determination of stability constants of metal chelates. Schubert and his coworkers (89, 90, 91) were among the first to utilize this method. The basis for this method

is essentially the measurement of the partition of the uncomplexed ion between the resin phase and the solvent phase in the presence of or in the absence of some complexing agent. At equilibrium, the amount of cation attached to the cation exchanger is proportional to the concentration of free ions in solution. It is a rapid and accurate method and needs only a very low concentration of the metallic ion. Furthermore, it can be utilized over a wide range of pH and temperature values.

(3) Optical and Spectroscopic Methods

Studies of the absorption spectra of metal chelates in the visible and ultraviolet regions give useful information about equilibria occuring within the solution. Whenever Beer's law is valid, optical density measurements may be employed to determine the relative concentrations of chelate in solution. The only requirement is that there is no (or at least very little) interference in the wavelength region being used for the measurement. This method can also be used to determine the concentration of the bound and unbound chelating agent or metal ions in solution.

(4) Polarography

It is possible to apply polarographic measurements to the studies of equilibria involving metal chelates (44, 69). Generally, the reduction potential of a metal at the dropping mercury electrode is shifted towards a more negative value during chelate formation or metal complexation. Stability and formation constants can be computed from potential and concentration measurements under a certain set of conditions.

(5) Solubility

Keefer (58, 59, 60, 61), Failey (47), and LaMer (66) have used the

increase in the solubility of a sparingly soluble salt in aqueous media containing the complexing agent or chelating anions as the basis for the determination of the stability of amino acid complexes.

(6) Reaction Kinetics

Reaction rates have been used by Taube (102, 103, 104) for the data needed in the determination of stability constants. Complexation can be followed by the calculation of the measurable rate of decomposition or association of the species involved.

(7) Electrical Conductance

Electrical conductance measurements furnish a convenient method for investigating the interaction of ions in both aqueous and non-aqueous media and hence can be employed in the determination of the formation constants of coordination complexes (12, 64).

(8) Other Miscellaneous Methods

Electrophoresis (74), biological assay (53), displacement reactions (33), liquid-liquid partition (65), freezing point depression, boiling point elevation and vapor pressure lowering (5), dielectric polarization (28), magnetic susceptibility (42), calorimetry (34), ultrasonic absorption (38, 72), ultracentrifugation (25), dialysis and filtration (46, 62, 63, 97), and light scattering (29, 45) metnods have all been used in the study of the stability of chelates and metal complexes.

Of all the methods described above, the potentiometric method best lends itself to the study of the formation constants of coordination complexes because it possesses certain inherent advantages not found in the other techniques:

(1) it allows the system under investigation to be homogeneous, not heterogeneous, as in ion exchange and liquid partition techniques.

(2) it directly measures a property (the EMF, from which can be determined the ionic strength) of the particular ion involved

(3) it does not alter or disturb the equilibrium being studied, either through the method itself or from the measurements that are taken.

CHAPTER II

THEORY

The theoretical basis of the computational method used in calculating the stepwise formation constants (K_1, K_2) reported in this dissertation is due to Bjerrum (4). At first, we shall summarize the essential features and the final formulations developed in Bjerrum's method for the computation of the stepwise formation constants. A more detailed algebraic treatment of Bjerrum's method will be given in the subsequent sections of this chapter.

Bjerrum's method provides a straight-forward means of computing the step formation constants, either graphically or analytically, from the knowledge of a single variable in solution. This variable is the concentration of the uncomplexed (unbound) ligand (C_L) in the solution containing the complex, the metal ion and the unbound ligand at equilibrium. The method requires computation of $\bar{n}$, the average number of ligands per central metal ion (cf. equations (3) to (8); explicit forms of the equations are given in the detailed section later in this chapter), and its derivative, $d\bar{n}/dC_L$, which is normally graphically computed (cf. equation (19a). Finally, it is possible to express all the formation constants in terms of C_L, $\bar{n}$, and $d\bar{n}/dC_L$ (cf. equation (42). A more convenient method, however, is to read the values of the step formation constants directly from a plot of $\bar{n}$ versus pC_L (cf. equation 28; figure 6).

Experimental determination of the unbound ligand concentration C_L is relatively simple when the precursor of the ligand is a protic acid HA, in which case C_L is designated by C_A, the concentration of the

unbound ligand anion. A potentiometric method employing a hydrogen electrode gives a direct measure of the solvated hydrogen ion concentration, the value of which can then be used to compute the concentration of the unbound ligand as follows:

$$S = \underset{\text{undissociated}}{HA} + \underset{\text{dissociated}}{A^-} \qquad \text{(i)}$$

$$HA \rightleftharpoons H^+ + A^- \qquad \text{(ii)}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{(iii)}$$

$$HA = \frac{[H^+][A^-]}{K_a} \qquad \text{(iv)}$$

Substitution of equation (iv) into equation (i) yields, upon rearrangement,

$$A^- = \frac{S}{\frac{[H^+]}{K_a} + L} = \frac{S \cdot K_a}{[H^+] + K_a} \qquad \text{(v)}$$

Detailed Algebraic Treatment of Bjerrum's Method for the Computation of Stepwise Formation Constants

The algebraic treatment which follows is due to Sen (92).

(a) Degree of Formation

Consider the following equilibria which correspond to a step system consisting of a central group (metal) M and N ligands L:

$$\begin{aligned} M + L &= ML \\ ML + L &= ML_2 \\ ML_2 + L &= ML_3 \qquad (1) \\ &\cdots\cdots\cdots\cdots \\ ML_{N-1} + L &= ML_N \end{aligned}$$

Therefore, the step formation constants corresponding to each of the above equilibria can be represented by

$$K_1 = \frac{C_{ML}}{C_M \cdot C_L}$$

$$K_2 = \frac{C_{ML_2}}{C_{ML} \cdot C_L}$$

$$K_3 = \frac{C_{ML_3}}{C_{ML_2} \cdot C_L}$$

.....

$$K_N = \frac{C_{ML_N}}{C_{ML_{N-1}} \cdot C_L} \qquad (2)$$

By definition, the degree of formation of the system is given by

$\bar{n}$ = Average number of ligands L attached per central group M

$$= \frac{\text{Total number of ligands L bound to M}}{\text{Total number of M present in the system}}$$

$$= \frac{\text{Total concentration of ligand A bound to M}}{\text{Total concentration of M in the system}} \qquad (3)$$

Total concentration of ligand L bound to M

$$= C_{ML} + 2C_{ML_2} + 3C_{ML_3} + ... + NC_{ML_N}$$

$$= K_1 \cdot C_M \cdot C_L + 2K_2 \cdot C_{ML} \cdot C_L + 3K_3 \cdot C_{ML_2} \cdot C_L ....$$

$$.... + NK_N \cdot C_{ML_{N-1}} \cdot C_L$$

Eliminating the term C_{ML_n} (n = 1, 2, 3, ... N-1) from the above relation with the help of equation (2), the total concentration of Ligand L bound to M

$$= C_M (K_1 \cdot C_L + 2K_1K_2C_L^2 + 3K_1K_2K_3C_L^3 + ...+ NK_1K_2K_3..K_NC_L^N) \qquad (4a)$$

Total concentration of M

$$= C_M + C_{ML} + C_{ML_2} + C_{ML_3} + ... + C_{ML_N}$$

$$= C_M + K_1C_M \cdot C_L + K_2C_{ML} \cdot C_L + K_3C_{ML_2} \cdot C_L + ... + K_NC_{ML_{N-1}} \cdot C_L$$

Again eliminating C_{ML_n} terms from the above, the total concentration of

$$M = C_M (1 + K_1C_L + K_1K_2 C_L^2 + K_1K_2K_3C_L^3 + \ldots + K_1K_2K_3\ldots K_NC_L^N) \quad (4b)$$

Therefore, dividing Equation (4a) by (4b), we obtain

$$\bar{n} = \frac{K_1C_L + 2K_1K_2C_L^2 + 3K_1K_2K_3C_L^3 + \ldots + NK_1K_2K_3\ldots K_NC_L^N}{1 + K_1C_L + K_1K_2C_L^2 + K_1K_2K_3C_L^3 + \ldots + K_1K_2K_3\ldots K_NC_L^N} \quad (5)$$

Since Equation (5) is quite unwieldly in its present form, a more abridged and less lengthy way of writing relations (3) and (5) is sought, in order to retain the usefulness of these equations. They are as follows: The statement of the definition of $\bar{n}$ given by relation (3) may be written in the following manner:

$$\bar{n} = \frac{\sum_{n=1}^{N} nC_{ML_n}}{C_M + \sum_{n=1}^{N} C_{ML_n}} \quad (6)$$

Relation (5) may be formulated as follows:

$$\bar{n} = \frac{\sum_{n=1}^{N} nC_L^n \prod_{n=1}^{N} K_n}{1 + \sum_{n=1}^{N} C_L^n \prod_{n=1}^{N} K_n} \quad (7)$$

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta_nC_L^n}{1 + \sum_{n=1}^{N} \beta_nC_L^n} \quad (8)$$

Where Σ stands for the summation of all of the terms after substituting for n all of the values between 1 and N, inclusive, and II stands for the product of all of the terms after substituting for n all of the values between 1 and N, inclusive. For example,

$$\prod_{n=1}^{3} K_n = K_1K_2K_3 = \beta_3$$

Thus, we can see that

$$n = f(C_L) \tag{9}$$

where C_L = free ligand concentration.

It must be emphasized that if the ligand is the anion of a weak acid (i.e., HA), C_L denotes the concentration of this free anion (ligand) A^- and would therefore be equal to C_A. Thus, we can now write

$$\bar{n} = \frac{TC_{MA} - C_A}{TC_M} \tag{10}$$

where TC_{MA} = total analytical concentration of HA

TC_M = total analytical concentration of central group (metal) M in the system.

Therefore, the experimental determination of $\bar{n}$ involves only the accurate determination of C_A.

(b) General Equations

It can be shown (92) in the case of a unidentate ligand that statistical considerations alone require

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} \tag{11}$$

In the case of a bidentate ligand, the quotient on the right-hand side of equation (11) must also be multiplied by another weighing factor, which is dependent upon the geometry of the complex. In order to account for the non-statistical forces, Bjerrum (4) introduced a spreading factor x, such that

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} x^2 = fx^2 \tag{11a}$$

The spreading factor x is a constant quantity for the whole system and

may assume any value between zero and infinity. Its value is chosen so that the ratio between the constants is just statistical for x = 1. It can be shown (92) that the validity of Equation (11a) is general for N = 2, while it also holds true for N = 3, providing that the formation curve is symmetrical. Thus, for the special case when N = 2, we see that

$$\frac{K_1}{K_2} = 4x^2$$

and when N = 3, it follows that

$$\frac{K_1}{K_2} = 3x^2 \qquad \text{and} \qquad \frac{K_2}{K_3} = 3x^2$$

To obtain the greatest possible symmetry, it is necessary to introduce an average formation constant K_{av} such that

$$K_n = \frac{N - n + 1}{n} \cdot K_{av} \cdot x^{(N - 2n + 1)} \tag{12}$$

Therefore,

$$\beta_n = K_1K_2K_3 \cdot \ldots K_n = {}^{N}C_n \cdot K_{av}{}^{n} \cdot x^{n(N-n)} \tag{13}$$

where

$${}^{N}C_n = \frac{N!}{(N - n)!\ n!}$$

when

$$n = N$$

$$\beta_N = K_{av} = K_{av}{}^{N} \tag{14}$$

because $${}^{N}C_N = 1 \quad \text{and} \quad x^o = 1$$

Thus when N = 2 and N = 3, respectively,

$$K_{av} = K_1K_2 = K_{av}{}^{2} \tag{15a}$$

$$K_{av} = K_1K_2K_3 = K_{av}{}^{3} \tag{15b}$$

Substituting the value of β_n from Equation (13) into Equation (8), we

obtain the following expression for $\bar{n}$:

$$\bar{n} = \frac{\sum_{n=1}^{N} n \cdot {}^{N}C_{n} \cdot K_{av}{}^{n} \cdot x^{n(N-n)} \cdot C_A{}^{n}}{1 + \sum_{n=1}^{N} {}^{N}C_{n} \cdot K_{av}{}^{n} \cdot x^{n(N-n)} \cdot C_A{}^{n}} \tag{16}$$

When expanded, Equation (16) is as follows:

$$\frac{N \cdot K_{av} \cdot x^{(N-1)} \cdot C_A + 2 \cdot \frac{N!}{(N-2)!2!} \cdot K_{av}{}^{2} \cdot x^{2(N-2)} \cdot C_A{}^{2} + 3 \cdot \frac{N!}{(N-3)!3!} \cdot K_{av}{}^{3} \cdot x^{3(N-3)} \cdot C_A{}^{3} + \ldots + N \cdot K_{av}{}^{N} \cdot C_A{}^{N}}{1 + N \cdot K_{av} \cdot x^{(N-1)} \cdot C_A + \frac{N!}{(N-2)!2!} \cdot K_{av}{}^{2} \cdot x^{2(N-2)} \cdot C_A{}^{2} + \frac{N!}{(N-3)!3!} \cdot K_{av}{}^{3} \cdot x^{3(N-3)} \cdot C_A{}^{3} + \ldots + K_{av}{}^{N} \cdot C_A{}^{N}} \tag{17}$$

It can be shown that for $\bar{n} = N/2$, the solution for the formation function (that is, the solution of the above equation) is

$$K_{av} = \frac{1}{C_A} \tag{18}$$

That is, in the formation curve (a plot of $\bar{n}$ versus $-\log C_A = pC_A$) the value of pC_A corresponding to $\bar{n} = N/2$ is equal to $\log K_{av}$. This in turn corresponds to the value of pC_A at the midpoint of the formation curve. Equation (8) may be written as follows:

$$\bar{n}\left(1 + \sum_{n=1}^{N} \beta_n C_A{}^{n}\right) = \sum_{n=1}^{N} n\beta_n C_A{}^{n} \tag{19a}$$

Differentiating with respect to C_A, we obtain

$$\frac{d\bar{n}}{dC_A}\left(1 + \sum_{n=1}^{N} \beta_n C_A{}^{n}\right) + \bar{n} \sum_{n=1}^{N} n\beta_n C_A{}^{n-1} = \sum_{n=1}^{N} n^2 C_A{}^{n-1} \tag{19b}$$

The slope of the formation curve (a plot of $\bar{n}$ versus $-\ln C_A$) is defined by the logarithmic relationship

$$S = \frac{d\bar{n}}{d \ln C_A} = -0.4343 \frac{d\bar{n}}{dpC_A} \tag{20a}$$

Equation (19b) is now rearranged to read

$$\frac{d\bar{n}}{dC_A} = \frac{\sum_{n=1}^{N} n^2 \beta_n C_A^{n-1} - \bar{n} \sum_{n=1}^{N} n \beta_n C_A^{n-1}}{1 + \sum_{n=1}^{N} \beta_n C_A^{n}} \qquad (19c)$$

$d\bar{n}/dC_A$ is now converted to $\delta = d\bar{n}/d \ln C_A$ through the following algebraic transformation:

Let $\ln C_A = y$; then by the Chain Rule of differential equations,

$$\frac{d\bar{n}}{dC_A} = \frac{d\bar{n}}{dy} \cdot \frac{dy}{dC_A} = \frac{d\bar{n}}{d \ln C_A} \cdot \frac{d \ln C_A}{dC_A} = \frac{d\bar{n}}{d \ln C_A} \cdot \frac{1}{C_A}$$

Therefore, by multiplying Equation (19c) throughout by C_A, $d\bar{n}/dC_A$ is transformed into , the slope of the formation curve. By doing so, we now obtain

$$\delta = \frac{\sum_{n=1}^{N} n(n - \bar{n}) \beta_n C_A^{n}}{1 + \sum_{n=1}^{N} \beta_n C_A^{n}} \qquad (20b)$$

The value of $\bar{n}$ from Equation (16), is now substituted into Equation (20b) in order to obtain a general relation connecting the slope of the formation curve and the spreading factor introduced by Bjerrum.

If we now confine ourselves to consider the slope γ of the midpoint (where $\bar{n} = N/2$) of the curve, this seemingly formidable general equation connecting δ and x becomes very simple and x may be readily calculated. At the midpoint

$$\bar{n} = \frac{N}{2} \qquad \text{and} \qquad K_{av} = \frac{1}{C_A} \text{ (cf. Eq. 18)}$$

and also

$$= \frac{\sum_{n=1}^{N} n(n - \frac{N}{2})\ {}^{N}C_{n} \cdot x^{n(N-n)}}{1 + \sum_{n=1}^{N} {}^{N}C_{n} \cdot x^{n(N-n)}} = \text{slope of the midpoint} \qquad (21)$$

For N = 1, $\gamma = 1/4$ (22a)

For N = 2, $\gamma = 1/(1 + x)$ (22b)

For N = 3, $\gamma = \frac{9 + 3x}{4(3x + 1)}$ (22c)

Equations (22b) and (22c) may be rearranged to read as follows:

$$x = \frac{1 - \gamma}{\gamma}, \text{ for } N = 2 \qquad (22d)$$

$$x = \frac{9 - 4\gamma}{12\gamma - 3}, \text{for } N = 3 \qquad (22e)$$

Thus, by knowing the average ionization constant, $K_{av} = 1/C_A$ (cf. Equation 18) at the midpoint (where $\bar{n} = N/2$) of the plot obtained by graphing $\bar{n}$ versus $-\ln C_A$, and the spreading factor x from Equations (21), (22d), and (22e), which relate the spreading factor x to the midpoint slope γ of the $\bar{n}$ versus $-\ln C_A$ plot, it should be possible to compute the values of the step constant by means of Equation (12):

$$K_n = \frac{N + n + 1}{n} \cdot K_{av} \cdot x^{(N - 2n + 1)} \qquad (12)$$

(c) Method of Graphical Solution

The method of graphical solution of the formation constants will now be discussed. The pertinent equation, Equation (5), is rearranged to read as follows:

$$(1 - \bar{n})K_1C_A + (2 - \bar{n})K_1K_2C_A^{\,2} + (3 - \bar{n})K_1K_2K_3C_A^{\,3} + \ldots$$

$$+ (n - \bar{n})K_1K_2K_3\ldots K_nC_A^{\,n} = \bar{n} \qquad (23)$$

It is quite obvious from the above relation that for any value of n (the sequence number of the formation constant) and N (the co-ordination

number), any one of the formation constants may be expressed in terms of the others. Thus

$$K_n = \frac{1}{C_A}\left[\frac{\bar{n}}{(n-\bar{n})\,K_1K_2K_3\ldots K_{n-1}\cdot C_A^{n-1}} + \frac{(\bar{n}-1)}{(n-\bar{n})\,K_2K_3\ldots K_{n-1}C_A^{n-2}} + \right.$$

$$\frac{(\bar{n}-2)}{(n-\bar{n})K_3K_4\ldots K_{n-1}C_A^{n-3}} + \frac{(\bar{n}-3)}{(n-\bar{n})K_4\ldots K_{n-1}C_A^{n-4}} + \ldots.$$

$$\left. + \frac{(n-n+1)}{(n-\bar{n})}\right] \qquad (24)$$

The spreading factor has been defined by Equation (11) and is a constant for the entire system. We may therefore write

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} = f_{n/n+1}\cdot x^2 \qquad (11)$$

Hence,

$$\begin{aligned} K_1/K_2 &= f_{1/2}\cdot x^2 \\ K_2/K_3 &= f_{2/3}\cdot x^2 \\ K_3/K_4 &= f_{3/4}\cdot x^2 \\ &\ldots\ldots\ldots\ldots \\ K_n/K_{n+1} &= f_{n/n+1}\cdot K_n \end{aligned} \qquad (25)$$

Combining the above

$$K_1 = f_{1/2}\cdot f_{2/3}\cdot f_{3/4}\cdot\cdots\cdot f_{n-1/n}\cdot x^{2(n-1)}\cdot K_n \qquad (26)$$

Substituting Equation (26) in (25),

$$K_2 = f_{2/3}\cdot f_{3/4}\cdot\cdots\cdot f_{n-1/n}\cdot x^{2(n-1)-2}\cdot K_n \qquad (27)$$

By a similar process of successive substitution, all of the K values may be expressed in terms of any one of them. These values of K_1, K_2, K_3, etc., may be substituted in the term within the bracket of the right-hand side of Equation (24). In the resulting equation, for large values of x (e.g., 100), and $\bar{n} = n - 1/2$, all terms except the last term (that of $(\bar{n}-n+1)/(n-\bar{n})$ within the bracket) become exceedingly small and

may therefore be neglected. The last term becomes equal to 1, and hence the K_n becomes equal in value to $1/C_A$. This means that if we have a plot of $\bar{n}$ versus pC_A, then log K_n is equal to pC_A corresponding to $\bar{n} = n - 1/2$. Therefore,

$$\begin{aligned} \log K_1 &= pC_A \text{ corresponding to } \bar{n} = 0.5 \\ \log K_2 &= pC_A \text{ corresponding to } \bar{n} = 1.5 \\ \log K_3 &= pC_A \text{ corresponding to } \bar{n} = 2.5 \\ \log K_n &= pC_A \text{ corresponding to } \bar{n} = n - 1/2 \end{aligned} \tag{28}$$

Thus log K_1, log K_2, log K_3, ... log K_n may be directly read from the formation curve. It should be realized at this point that the above is true only when x is large; this fact forms the basis for the graphical determination of the K values. The relations so far developed are for unidentate ligands. We have already seen that these relations are in general true for N = 2 and N = 3 in the case of a symmetrical formation curve. Because a large majority of the metals which form complexes have coordination numbers of four or six, and because the bidentate ligands constitute the most important group of organic ligands, the extension cases of N = 2 and N = 3 will be specifically considered.

The case of N = 2

The important relations developed thus far are summarized as follows:

$$\bar{n} = \frac{K_1C_A + 2K_1K_2C_A^2}{1 + K_1C_A + K_1K_2C_A^2} \quad \text{(cf. Eq. 5)} \tag{29}$$

$$K_1/K_2 = 4x^2 \quad \text{(cf. Eq. 11)} \tag{30}$$

$$K_1 \cdot K_2 = K_{ov} = K_{av}^2 \quad \text{(cf. E.q. 14)} \tag{31}$$

$$K_{av} = \left(\frac{1}{C_A}\right)_n = \frac{N}{2} = 1 \quad \text{(cf. Eq. 18)} \tag{32}$$

$$K_1 = 2K_{av} \cdot x; \; K_2 = \frac{K_{av}}{2x} \quad \text{(cf. Eq. 12)} \tag{33}$$

$$\bar{n} = \frac{2K_{av} \cdot x \cdot C_A + 2K_{av}^2 \cdot C_A^2}{1 + 2K_{av} \cdot x \cdot C_A + K_{av}^2 \cdot C_A^2} \quad \text{(cf. Eq. 16 and Eq. 17)} \qquad (34)$$

The midpoint slope of the formation curve is then given by

$$\gamma = \frac{1}{1 - x} \text{ (cf. Eq. 21 and Eq. 22b) and } x = \frac{1 - \gamma}{\gamma} \text{ (cf. Eq. 22d)} \qquad (35)$$

The validity of Equation (28) may be shown by substitution of Equation (3) into Equation (29), again considering that x is large and recalling that $\bar{n} = n - 1/2$.

Substitution of Equations (32) and (22d) into (33) yields

$$K_1 = \left(\frac{1}{C_A}\right)\bar{n} = 1 \cdot \left(\frac{1 - \gamma}{\gamma}\right) \quad \text{and} \quad K_2 = 1/2 \cdot \left(\frac{1}{C_A}\right) n \qquad (36)$$

The case of N = 3

$$\bar{n} = \frac{K_1C_A + 2K_1K_2C_A^2 + 3K_1K_2K_3C_A^3}{1 + K_1C_A + K_1C_A + K_1K_2C_A^2 + K_1K_2K_3C_A^3} \qquad (37)$$

$$K_1/K_2 = 3x^2; \; K_2/K_3 = 3x^2 \text{ (cf. Eq. 11)} \qquad (38)$$

$$K_1K_2K_3 = K_{ov} = K_{av}^3$$

$$K_{av} = \left(\frac{1}{C_A}\right)_n = \frac{N}{2} = 1.5 \text{ (cf. Eqs. 14 and 18)} \qquad (39)$$

$$K_1 = 3K_{av} \cdot x^2; \; K_2 = K_{av}; \; K_3 = 1/3 \cdot \frac{K_{av}}{x^2} \text{ (cf. Eq. 12)} \qquad (40)$$

Equations (16) and (17) reduce to

$$\bar{n} = \frac{3 \cdot K_{av} \cdot x^2 \cdot C_A + 6 \cdot K_{av}^2 \cdot x^2 \cdot C_A^2 + 3 \cdot K_{av}^3 \cdot C_A^3}{1 + 3 \cdot K_{av} \cdot x^2 \cdot C_A + 3 \cdot K_{av}^2 \cdot x^2 \cdot C_A^2 + K_{av}^3 \cdot C_a^3} \qquad (41)$$

and recalling

$$x = \frac{9 - 4\gamma}{12\gamma - 3} \qquad (22e)$$

Substitution of Equations (39) and (22e) into (40) yields

$$K_1 = 3\left(\frac{1}{C_A}\right)_{\bar{n}} = 1.5 \cdot \left(\frac{9 - 4}{12 - 3}\right)^2$$

$$K_2 = \left(\frac{1}{C_A}\right)_{\bar{n}} = 1.5 \qquad (42)$$

$$K_3 = 1/3\left(\frac{1}{C_A}\right)_{\bar{n}} = 1.5 \cdot \left(\frac{12Y - 3}{9 - 4Y}\right)^2$$

Thus we have been able to demonstrate the method of graphical solution of formation constants and also their computation by means of Equations (12), (36), and (42) when the values of the average formation constant K_{av} and the spreading factor x have been evaluated from the formation curve.

CHAPTER III

EXPERIMENTAL

Cells, Bridge, Electrodes and Constant Temperature Bath

Electrolytic cells of the type

Pt, H_2 (P atm.) | HA (m), Organic Solvent (X), Water (Y) ‖ KCl (saturated) | Hg_2Cl_2 - Hg I

were employed in all experimental determinations of the ionization constants of the weak acids, whereas the cells of the type

Pt, H_2(P atm.) | HA (m_1), $M(NO_3)_2$ (m_2), $NaNO_3$ (m_3), HNO_3 (m_4), Organic Solvent (X), Water (Y) ‖ KCl (saturated) | Hg_2Cl_2 - Hg II

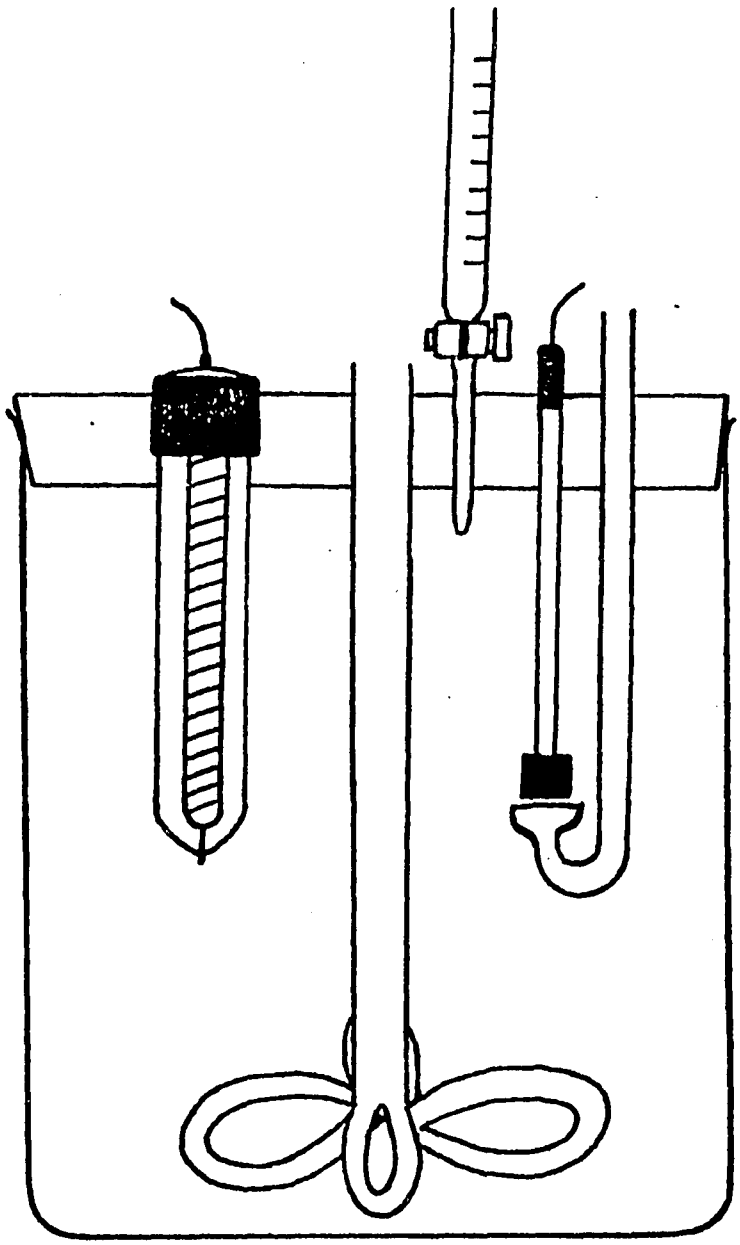
were used for the determination of the formation constants of the lactic acid complexes of Ca^{2+} and Zn^{2+} ions. For the determination of the formation constants of the complexes containing Fe^{3+} as the central metal ion, $Fe(ClO_4)_3$ was substituted for $M(NO_3)_2$ as the source of the metal ions, and the buffer pair of $NaClO_4$ - $HClO_4$ was used in place of the $NaNO_3$ - HNO_3 in cell II.

The basic cell design employed in this study is depicted in Figure 2. One hydrogen electrode and one Saturated Calomel Electrode (SCE) were coupled in each individual cell, of which there were four replicates. Thus, it was made possible for four separate readings to be taken concurrently, and since two different constant temperature baths were made available into which these cells could be placed, two readings could be made at one temperature while the other two were made at a different temperature.

The electromotive force of each cell was measured by a Leeds and Northrup K-3 type Universal Potentiometer calibrated against an Eppley

FIGURE 2:

DIAGRAM OF EXPERIMENTAL CELL



unsaturated-type Weston Standard Cell. Null detector readings were obtained using a sensitive (0.004 μa/mm) Rubicon galvanometer. The SCE employed was a Corning No. 476002 Calomel reference electrode with an asbestos fiber liquid junction, suitable for operation over a wide temperature range (from - 50°C to + 80°C).

The hydrogen electrodes were prepared from Sargent No. 5-30505 platinum foil electrodes which had been cleansed first by rapid immersion in fifty per cent aqua regia (prepared by mixing three volumes of concentrated hydrochloric acid (approximately 12 M), one volume of concentrated nitric acid (approximately 15 M) and four volumes of distilled water). After thoroughly rinsing with doubly distilled water, the electrodes were coated with a thin layer of platinum black, which had been prepared according to a procedure suggested by Bates (3):

One and one-half grams of scrap platinum was cleaned in hot concentrated nitric acid, rinsed with distilled water, and ignited in a Bunsen flame. The metal was cut into small fragments to facilitate dissolution and was digested in warm aqua regia (a mixture of three volumes of concentrated hydrochloric acid (approximately 12 M) with one volume of concentrated nitric acid (approximately 15 M) until it was completely dissolved. The acidic platinum solution was evaporated to dryness on a steam bath and the residue was taken up in about 20 ml. of concentrated hydrochloric acid. The evaporation and addition of hydrochloric acid were repeated twice. The residue of chloroplatinic acid hexahydrate, $H_2PtCl_6 \cdot 6H_2O$, which remained after a fourth evaporation on the steam bath, was dissolved in 100 ml. of doubly distilled water, and 80 mg. of lead acetate was added. When properly prepared, this amber solution should be perfectly clear; in order to retard decomposition, it was

stored in a dark glass bottle fitted with a ground-glass stopper.

Bates (3) has also provided us with a convenient method for the electrodeposition of platinum black onto the electrode surface. The platinization procedure makes use of the chloroplatinic acid solution that was previously prepared, and involves the passage of a current of 200 to 400 ma. for one to three minutes in such a direction that the Pt electrode to be coated is the cathode. A similar platinum electrode serves as the anode.

When the same platinizing solution is used repeatedly, the current efficiencies decrease as the platinum is depleted, so that precise control of the current does not necessarily insure the production of satisfactory hydrogen electrodes. But, on the other hand, if the platinum solution is properly prepared, the conditions of electroplating are not that critical. It appears (3) that the best guide is the appearance of the finished Pt electrode itself. The surface coating of platinum black should appear uniform and black, without any streaking on the surface. The presence of lead (in the form of lead acetate) causes a smooth and adherent layer of platinum black to be deposited (3).

The finished hydrogen electrodes were intercompared, and those M_2 electrodes which did not agree within $\pm$ 0.01 millivolts of each other were discarded. The satisfactory electrodes were kept immersed in doubly distilled water and remained effective for a period of several months.

A Sargent Thermonitor control, along with a Sargent Water Bath Cooler, provided temperature settings of 15°C, 25°C, 35°C, and 40°C of the constant temperature bath with a precision of $\pm$ 0.1°C.

Chemicals and Solutions

The doubly-distilled water was obtained by distilling distilled water which had previously been run through an ion-exchanger. Figure 3 is a diagram of the apparatus used in distillation, which consisted of an all-glass still containing a column 36 inches high and 1.5 inches in diameter, filled at alternate levels with glass beads and 2 cm. lengths of 4 mm. glass tubing. The conductivity of this water was 3.3×10^{-6} mho/cm., as determined by means of a Leeds and Northrup Model 4866 Conductance Bridge. Wherever the term "distilled water" appears in this dissertation, it will refer to water that has been prepared in the above manner.

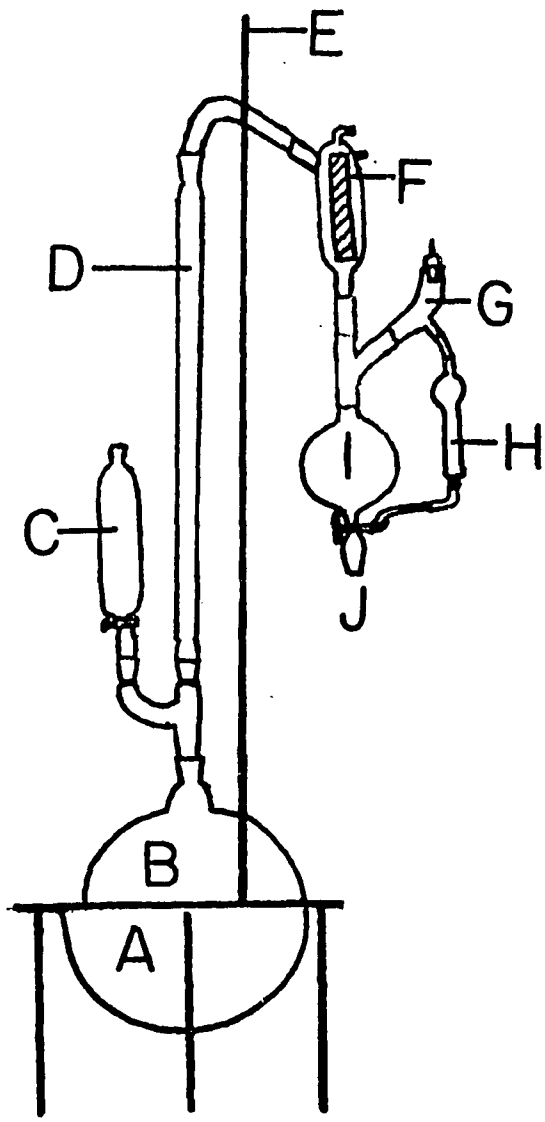
The lactic acid was purified by means of an abbreviated version of the method developed by Borsook, Huffman and Liu (40), which involved the vacuum distillation of impure lactic acid at 12 mm. Hg, followed by the recrystallization of the 119°C fraction from xylene at 15°C.

Commercially available absolute ethanol and methanol were found to be sufficiently pure by gas chromatography and were used without any further purification. The methanol used was of Malinckrodt Analytical Reagent grade; the absolute ethanol was of USI Reagent Quality. The glucose used in our work was anhydrous d-glucose $[\alpha]_D^{20} = + 52.2 \pm 0.5$, which was purchased from the Nutritional Biochemical Corporation. It was USP grade, and contained as impurities ash, 0.05%; moisture, 0.5%; and iron, 0.0017%. The nitric acid (15M) was Mallinckrodt Analytical Reagent grade and the perchloric acid was 70-72% ACS-certified reagent grade purchased from Curtin.

The 0.01 M stock solutions of Ca^{2+}, Fe^{3+}, and Zn^{2+} ions were prepared from $Ca(NO_3)_2$, $Fe(ClO_4)_3$, and $Zn(NO_3)_2$, respectively. A

FIGURE 3:

DIAGRAM OF DISTILLATION APPARATUS


E
F
D
G
H
I
C
J
B
A

LEGEND TO

FIGURE 3:

A. HEATING MANTLE

B. 3-liter ROUND BOTTOM FLASK

C. CYLINDRICAL SEPARATORY FUNNEL WITH STOPCOCK

D. DISTILLATION COLUMN, PACKED WITH GLASS BEADS AND SMALL LENGTHS OF GLASS TUBING

E. ATMOSPHERIC VENT TUBE

F. "COLD-FINGER" CONDENSATION TUBE

G. SIDE-ARM ADAPTER FITTED WITH GROUND-GLASS STOPPER

H. CALCIUM CHLORIDE DRYING TUBE

I. COLLECTOR VESSEL

J. 3-WAY STOPCOCK (OPEN TO ATMOSPHERE)

sufficient amount of the HNO_3 was added to the calcium and zinc nitrate stock solutions to render them both 1×10^{-4} N with respect to the acid; the ferric perchlorate solution was brought to an acid strength of 1×10^{-2} N by addition of $HClO_4$.

Standardization of Solutions

The stock salt solutions were standardized according to standard procedures. Calcium was determined gravimetrically (17) by precipitating as calcium oxalate, and then weighing as $CaC_2O_4 \cdot H_2O$ after drying to a constant weight. A measured quantity of $Ca(NO_3)_2$ solution, containing approximately 0.2 g. of calcium, was taken in a 400 ml. beaker provided with a stirring rod, for the determination of calcium. The sample was diluted with 10 ml of distilled water and acidified with 15 ml of dilute (1:1) HCl. The solution was then cautiously brought to boiling and maintained at that temperature for several minutes in order to expel all dissolved CO_2. The sides of the beaker were then washed down with distilled water, and the volume of the solution was then adjusted to approximately 200 ml; a few drops of methyl red indicator were then added to the solution. The solution was next brought to boiling and a warm solution of 2 g. of anhydrous ammonium oxalate dissolved in 50 ml of distilled water was slowly added with stirring to the $Ca(NO_3)_2$ solution. Dilute (1:1) ammonium hydroxide was then added dropwise with stirring to the solution until it was neutral or faintly basic, as indicated by the color change (red to yellow) of the indicator. The mixture was then allowed to stand overnight at room temperature. After the precipitate had settled, the supernatant liquid was tested with a few drops of ammonium oxalate solution to insure completeness of the precipitation.

The precipitate was then transferred to a previously weighed sintered glass crucible, where it was washed with dilute (1:1) ammonium hydroxide. The precipitate was then dried in an oven for 1-2 hours at 100-115°C. It was placed in a dessicator for cooling for about 20 minutes, and was then weighed as $Ca(C_2O_4) \cdot H_2O$. The determinations were repeated and the strength of the stock solution found to be 0.01015 M with respect to $Ca(NO_3)_2$.

The standardization of the ferric ion stock solution involved its precipitation as hydrous ferric oxide from homogeneous medium (10); the hydrous ferric oxide was finally converted by ignition to anhydrous ferric oxide for weighing. A measured volume of the stock solution containing approximately 100 mg. of iron was taken for each determination. The solution was diluted with 50 ml. of distilled water, and 5 ml. of concentrated (12 M) HCl and 1-2 ml of concentrated (15 M) HNO_3 were added to the solution. The acidified solution was then boiled gently to expel any oxides of nitrogen. The solution was then diluted to 400 ml with distilled water, and was next treated with concentrated (15 M) NH_4OH with constant stirring until the appearance of a faint but permanent turbidity of the solution, due to the precipitation of the hydrous oxide. The precipitate was carefully dissolved and the solution rendered clear by the addition of a minimum volume of dilute (1:1) HCl. To this solution were then added 2 ml of concentrated formic acid, 15 g. of ammonium chloride and 4-5 g. of urea. The solution was then heated carefully and maintained at a gentle boil. Heating was continued until precipitation was judged complete. Toward the end of the heating period, about 5 ml of freshly prepared 3% hydrogen peroxide were added.

The suspension was filtered through an ashless filter paper (Whatman No. 42 Black Label). The precipitate was washed three times with 20-30 ml portions of hot 1% ammonium nitrate solution and these washings were decanted through the filter paper. The bulk of the precipitate was then quantitatively transferred. The precipitate remaining in the beaker was stirred with 75-100 ml of distilled water, which was heated nearly to boiling, and was completely with the addition of dilute (1:1) HNO_3. Aqueous ammonia was slowly added until the solution was definitely basic and the precipitate reappeared. The precipitate was then washed as before in the beaker by decantation before being transferred to the filter paper containing the bulk of the precipitate. The filter paper with the precipitate was then transferred to a porcelain crucible that had previously been ignited to a constant weight. The paper was charred at a lower temperature initially, and care was taken to allow for the free access of air. The temperature was gradually increased using a Meeker burner, until all of the carbon had been burned away. The crucible containing the charred filter paper was then ignited to a constant weight at 900° to 1000°C. These determinations were performed in triplicate, and the resulting concentration of the $Fe(ClO_4)_3$ stock solution was found to be 0.01040 M.

Standardization of Zinc Nitrate Solution

The zinc solution was standardized by precipitation of the Zn^{2+} ion as zinc 8-hydroxyquinolinate (30) from an acetic acid-ammonium acetate buffer medium. A measured volume of the stock solution, containing approximately 0.15 g. zinc, was diluted to 100 ml. The solution was then buffered by the addition of 5 g. of ammonium acetate and 4 g. of acetic acid. This solution was warmed to 60°C., and treated

with a slight excess of a 2% solution of 8-hydroxyquinoline in 2 N acetic acid, boiled a few minutes, then filtered through a previously weighed sintered glass crucible and washed with hot distilled water. The well-washed precipitate was dried at 130-140°C and then weighed as $Zn(C_9H_6ON)_2$, which contains 18.49% zinc. Triplicate determinations were made, with the resulting concentration of the $Zn(NO_3)_2$ being ascertained as equal to 0.0098 M.

Solvents

The methanol-water mixed solvents and ethanol-water mixed solvents used contained 90%, 80%, 70%, 50%, 30%, 20%, and 10% of the organic component. The glucose-water mixed solvents used were 0.01, 0.05, and 0.1 molal with respect to glucose. All of the solutions utilized in the potentiometric determinations of the pK_a's and log K_f's were prepared volumetrically from the various salt and acid stock solutions, solvents, and distilled water. The solutions and the solvents were normally dispensed from a burette or by a pipettd. Molar concentrations (molal in the case of the glucose-water mixed solvents) were converted to weight percentages by application of the appropriate density data.

E.M.F. Readings

The hydrogen gas used in these measurements was Matheson ultrapure hydrogen which was further purified by passing it through a Deoxo catalytic purifier prior to its entering the electrolytic cell. The hydrogen was saturated with the solution to be used in the cell by passage through a bubbler before actually entering the cell itself.

The procedure that was generally adhered to during the determinations of the ionization constants of lactic acid in the various

mixed solvent media was to first rinse the cell, the bubbler and the electrodes with the test solution. The cell and the bubbler were next filled with the solution, and the two electrodes were coupled and then introduced into the cell. The hydrogen was introduced to the cell bia the bubbler and bubbling began to commence within the cell almost instantaneously. Pressure was maintained at 20 p.s.i. and the flow rate of the hydrogen gas was kept regulated by means of a needle valve until three or four bubbles exited the bubbler each second. EMF readings were taken at approximately fifteen minute intervals until two subsequent values of the measured EMF agreed to within 0.2 millivolt of each other. It was then assumed that equilibrium had been attained.

About three to four hours were usually required for the initial equilibrium to be reached, although often less time was required. There appears to be a very sharp decrease in the cell voltage during the first hour and a more gradual decrease thereafter (27). After three to four hours, a steady decrease in the cell voltage is noted on the order of 0.01 mv per minute. It was assumed that the system remained in equilibrium once the steady state had been reached and that evaporation of the solvent was the cause of the gradual drop in cell EMF. Other systems appear to give similar results (95).

Titrations

Titrations were performed in order to determine the concentration of the unbound ligand and these data were then used to compute the formation constants of the various metal complexes. It was shown in the theory section (Chapter II) that the knowledge of the concentration of the unbound ligand was necessary for the computation of the formation constants of the complexes. The concentration of the unbound ligand

was found by titration of two nearly identical systems (to be described in the next paragraph) with standard sodium hydroxide solution.

It has been mentioned earlier that it was necessary to titrate a pair of solutions for the determination of the concentration of the unbound ligand in each of the cases studied. One of the solutions contained a measured amount of the metal ion, a measured excess of the ligand acid (lactic acid), and a precisely known amount of the free acid in an exactly known volume of the mixed solvent. The second solution was exactly similar to the first one, except that it did not contain any metal ion.

The first solution always contained 0.400 milliequivalents (0.036 g.) of lactic acid, 0.050 millequivalents of the metal ion, and an appropriate volume of the standard $NaNO_3$ solution ($NaClO_4$ in the case of iron) for adjusting the ionic strength (0.025, 0.050, 0.075, or 0.100). The final volume was adjusted to 100 ml by adding the appropriate mixed solvent. The second solution of the same pair was prepared identically, except that the volume (2.5 ml) of the standard solution of the metal ion was substituted by an equal volume of distilled water. After the neutralization of the lactic acid, the ionic strength increased slightly upon further addition of NaOH, but this effect is negligible except at high pH's (near 12 and above) (12).

In the studies leading to the calculations of the ionization constants of lactic acid itself, 0.2 molal, 0.1 molal, 0.05 molal, 0.01 molal, and 0.005 molal lactic acid in each of the compositions of the solvents described, were investigated.

The titrant was added in increments of 0.5 ml, and the titration was followed potentiometrically. EMF data were recorded after equili-

brium was reached, which was determined by applying the previously described criterion.

The titrant used was a 0.1 N solution of sodium hydroxide in an appropriate solvent. The solvent used was methanol, when the titration was performed in methanol-water systems; it was ethanol, when the titration was performed in ethanol-water systems; and it was water when the titration was performed in glucose-water systems. The titrant was standardized against potassium hydrogen phthalate, and the sodium hydroxide solution was always delivered from a 10 ml capacity microbutette.

Values for the S.C.E. standard potentials at various temperatures are given in Table I. They include the junction potential arising from the electrode being placed in an aqueous solution (3). As the titrations progress in mixed solvent media, these potentials will not be absolutely correct, due to an unknown change in the junction potential with a change in the solvent composition.

The EMF data that were obtained were corrected with respect to atmospheric pressure. Fluctuations in pressure of the magnitude of 25 millimeters can be shown (27) to cause no significant alteration in the calculated pH (i.e., it can be shown that a divergence of 127 mm Hg from the standard pressure is responsible for a fluctuation of only 2.3 mv., which corresponds to about 0.4 pH unit). The measured potentials could be estimated to within $\pm$ 0.5 millivolt, corresponding to an accuracy of $\pm$ 0.01 pH unit.

TABLE I

VALUES OF THE

STANDARD POTENTIAL, $(E_{S.C.E.} + E_j^w)$, FOR THE M_2

SATURATED CALOMEL CELL AT

VARIOUS TEMPERATURES (3)

Temperature, $^oC.$	$(E_{S.C.E.} + E_j^w)$, mv.
15	250.6
25	244.4
35	239.1
40	236.5

CHAPTER IV

RESULTS AND CALCULATIONS

It was shown in Chapter II that the successive formation constants of metal ion complexes may be expressed as functions of the unbound ligand concentrations. In the cases where the precursor of the ligand is a monoprotic acid of the type HA, it will be necessary to have the knowledge of the hydrogen ion concentration (solvated) of the system and the ionization constant of the monoprotic acid, in order to be able to calculate the concentration of the unbound ligand. Therefore, the primary experimental goal is to obtain a reliable measurement of the hydrogen ion concentration in the systems being studied.

Consider the cell

$$\text{Pt, } H_2 \text{ (P atm.)} \mid H^+ (a_{H^+}),\ A^- (a_{A^-}),\ \text{Organic (X)},\ H_2O \text{ (Y)} \parallel \text{KCl (saturated)} \mid Hg_2Cl_2 - Hg \qquad \text{III}$$

for which the cell potential is

$$F_{H_2} = E_{meas} - E_{S.C.E.} - E_j^m \qquad (43)$$

where F_{H_2} is the hydrogen electrode potential, E_{meas} is E.M.F. of the cell as measured experimentally, $E_{S.C.E.}$ is the potential of the saturated calomel electrode, and E_j^m is the liquid junction potential at the interface of the KCl solution (salt bridge) and the mixed solvent medium. From the Nernst equation, the potential of the hydrogen electrode of cell III is given by (27)

$$E_{H_2} = - \frac{2.303\ RT}{F} \log \frac{a_{H^+}}{P_{H_2}} 1/2 \qquad (44)$$

where the symbols have their usual significance. If we now wish to correct the value of E_{H_2} to unit atmospheric pressure, a correction

factor (3) of

$$\Delta E = \frac{2.303\ RT}{2\ F} \log \frac{760}{P_{H_2}} \tag{45}$$

must be added to E_{H_2}. The corrected potential is then given by

$$E_{corr} = E_{H_2} + \frac{2.303\ RT}{2\ F} \log \frac{760}{P_{H_2}} \tag{46}$$

Substitution for E_{H_2} in equation (46) with the expression for E_{H_2} from equation (43) gives

$$E_{corr} = E_{meas} - (E_{S.C.E.} + E_j^m) + \frac{2.303\ RT}{2\ F} \log \frac{760}{P_{H_2}} \tag{47}$$

It follows from equation (44) and equation (47) that

$$pH = \frac{E_{corr}F}{2.303\ RT} \tag{48}$$

In the current studies, a saturated calomel electrode in conjunction with a hydrogen electrode was used to measure E_{meas} from which E_{corr} and the pH of the medium were calculated using Equations (47) and (48). In the foregoing discussion, it has been tacitly assumed that the reference state is that of unit fugacity of the hydrogen gas and unit activity coefficient of the solvated hydrogen ion.

It is of intest to note here the difference between the foregoing reference state and the reference state in pure aqueous medium, since it is our objective to express the thermodynamic quantities studied in this investigation with respect to an aqueous reference state.

Consider the cell

Pt, H_2 (1 atm) | H^+ (m_1), H_2O || KCl (saturated) | Hg_2Cl_2-Hg IV

Assuming unit fugacity and unit activity coefficient, the potential of the cell is given by

$$E_{H^+(R)} = E_{S.C.E.} + \frac{2.303\ RT}{F} pH_{(R)} + E_j^w \tag{49}$$

We can say that when cell IV is the aqueous reference cell, equation (49) is true. Now consider the cell with the mixed solvent

$$\text{Pt, } H_2 \text{ (1 atm)} \mid H^+ (m_2), \text{ Organic (X), } H_2O \text{ (Y)} \parallel \text{KCl (saturated)} \mid Hg_2Cl_2 - Hg \qquad \text{(V)}$$

Again assuming unit fugacity and unit activity coefficient in the mixed solvent, the potential of cell V is given by

$$E_{H^+(X)} = E_{S.C.E.} + \frac{2.303\ RT}{F} pH_{(x)} + E_j^m \qquad (50)$$

Although unit activity coefficient has been assumed in both of the cells (IV and V), it is unlikely that $m_1 = m_2$, or $E_{H^+(R)} = E_{H^+(x)}$, or $pH_{(R)} = pH_{(x)}$. Rearrangement of equations (49) and (50) each gives, respectively,

$$\frac{2.303\ RT}{F} pH_{(R)} = E_{H^+(R)} - E_{S.C.E.} - E_j^w \qquad (51)$$

and $$\frac{2.303\ RT}{F} pH_{(x)} = E_{H^+(x)} - E_{S.C.E.} - E_j^m \qquad (52)$$

Subtracting equation (52) from equation (51), we obtain

$$\frac{2.303\ RT}{F} pH_{(R)} - \frac{2.303\ RT}{F} pH_{(x)} = E_{H^+(R)} - E_{H^+(x)} - E_j^w + E_j^m \qquad (53)$$

or,

$$\frac{2.303\ RT}{F} pH_{(R)} = \frac{2.303\ RT}{F} pH_{(x)} + E_{H^+(R)} - E_{H^+(x)} - E_j^w + E_j^m \qquad (54)$$

Equation (53) explicitly expresses the difference between $pH_{(R)}$ and $pH_{(x)}$ in two media, both of which are defined to be in their respective reference states; this difference is due to the primary medium effect, except for the small correction factor $(-E_j^w + E_j^m)$.

It is quite obvious that the hydrogen electrode potential calculated from equation (48) can be used to determine the pH of the lactic acid and its metal complexes in the mixed solvent systems being investigated. In order to do so, the corrected value of the hydrogen

pressure at the electrode surface must be known. The corrected pressure of hydrogen (12) is given by

$$P_{H_2} = P_{bar} - (P_S + P_w) + \frac{0.4\ h}{13.6} \qquad (55)$$

where P_{bar} is the barometric pressure in mm Hg, P_S is the partial pressure of the organic solvent, P_w is the partial pressure of the water, and h is the average depth of the jet of hydrogen in mm during titration (i.e., the distance between the ground-glass bubbler and the electrode surface). The partial pressures of the organic solvent and water were obtained from the vapor pressures of the pure solvents, methanol and ethanol, calculated from Schlessinger's equation (93):

$$\log P = (-0.2185\ A/K) + B \qquad (56)$$

where P is the vapor pressure of the pure solvent in mm Hg at temperature K (in ^{o}K), A is the molar heat of vaporization in cal/mole, and B is an empirically determined constant, dependent upon the temperature range under investigation. For pure methanol within the limits of $-44.0^{o}C$ to $224.0^{o}C$, A = 8978.8 and B = 8.639821; for absolute ethanol in the range of $-31.3^{o}C$ to $242.0^{o}C$, A has the value of 9673.9 and B is equal to8.827392. The vapor pressures of pure water at different temperatures were obtained from Bates (3). These vapor pressures of the pure solvents and of water were converted to the partial pressures of each of these liquids by use of Raoult's law (15), which takes the form

$$P_S = X_S \cdot P_S^o \qquad \text{and} \qquad P_w = X_w \cdot P_w^o \qquad (57)$$

where X_S and X_w represent the mole fractions of the organic solvent and water, respectively, and P_S^o and P_w^o are the vapor pressures of the pure liquids. The equations that were used to relate the weight percent concentrations of the test solutions to their corresponding mole

fractions are as follows:

$$TNMS = (WPS/GMWS) \quad \text{and} \quad TNMW = (WPW/GMWW) \tag{58}$$

where TNMS represents the total number of moles of solvent, TNMW is the total number of moles of water, WPS is the weight percent of the solvent, WPW is the weight percent of water, GMWS is the gram-molecular weight of the solvent, and GMWW is the gram-molecular weight of water. The sum of these equations

$$TNMS + TNMW = (WPS/GMWS) + (WPW/GMWW) = TNM \tag{59}$$

defines TNM, the total number of moles in the mixed solvent system. This quantity can be related to the respective mole fractions by the equations

$$XS = TNMS/TNM \quad \text{and} \quad XW = TNMW/TNM \tag{60}$$

The vapor pressures of pure water and absolute methanol and absolute ethanol, as well as their partial pressures and their mole fractions, at the various temperatures are given in Table II.

Once the pH values had been precisely determined through the use of equation (48), the ionization constants of lactic acid in various mixed solvent systems at four different temperatures were determined in the following manner:

Consider the monoprotic acid HA, whose ionization is given by the equilibrium:

$$HA \leftrightharpoons H^+ + A^-$$

The ionization constant for this simple, one step equilibrium is equal to

$$K_1 = \frac{[H^+][A^-]}{[HA]} \tag{61}$$

since for every H^+ formed from the ionization, there is also an A^- formed,

$$[H^+] = [A^-] \tag{62}$$

and also the concentration of the unionized lactic acid can be written

TABLE II

VAPOR PRESSURES OF PURE SOLVENTS; PARTIAL PRESSURES AND MOLE FRACTIONS OF VARIOUS AQUEOUS-ORGANIC MIXED SOLVENT MEDIA AT 15°C.

METHANOL-WATER

WT% MeOH	XS MeOH	P_S^o MeOH	P_w^o H_2O	P_S MeOH	P_w H_2O
10.00	0.059	67.85	12.80	3.99	12.05
20.00	0.123	67.85	12.80	8.36	11.22
30.00	0.194	67.85	12.80	13.18	10.31
50.00	0.360	67.85	12.80	24.42	8.19
70.00	0.568	67.85	12.80	38.51	5.54
80.00	0.692	67.85	12.80	46.97	3.94
90.00	0.835	67.85	12.80	56.66	2.11

ETHANOL-WATER

WT% EtOH	XS EtOH	P_S^o EtOH	P_w^o H_2O	P_S EtOH	P_w H_2O
10.00	0.042	32.20	12.80	1.34	12.27
20.00	0.089	32.20	12.80	2.87	11.66
30.00	0.144	32.20	12.80	4.62	10.96
50.00	0.281	32.20	12.80	9.06	9.20
70.00	0.477	32.20	12.80	15.37	6.69
80.00	0.610	32.20	12.80	19.65	4.99
90.00	0.779	32.20	12.80	25.08	2.83

GLUCOSE-WATER

WT% Glucose	XS Glucose	P_S^o Glucose	P_w^o H_2O	P_S Glucose	$P_w H_2O$
0.18	0.0002	0.00	12.80	0.00	12.80
0.89	0.0009	0.00	12.80	0.00	12.79
1.77	0.0018	0.00	12.80	0.00	12.78

TABLE II (CONT'D)

VAPOR PRESSURES OF PURE SOLVENTS; PARTIAL PRESSURES AND MOLE FRACTIONS OF VARIOUS AQUEOUS-ORGANIC MIXED SOLVENT MEDIA AT 25°C.

METHANOL-WATER

WT% MeOH	XS MeOH	P_S^o MeOH	P_w^o H_2O	P_S MeOH	P_w H_2O
10.00	0.059	114.80	23.80	6.75	22.40
20.00	0.123	114.80	23.80	14.15	20.87
30.00	0.194	114.80	23.80	22.30	19.18
50.00	0.360	114.80	23.80	41.33	15.23
70.00	0.568	114.80	23.80	65.15	10.29
80.00	0.692	114.80	23.80	79.47	7.32
90.00	0.835	114.80	23.80	95.86	3.93

ETHANOL-WATER

WT% EtOH	XS EtOH	P_S^o EtOH	P_w^o H_2O	P_S EtOH	P_w H_2O
10.00	0.042	59.00	23.80	2.46	22.81
20.00	0.089	59.00	23.80	5.26	21.68
30.00	0.144	59.00	23.80	8.47	20.38
50.00	0.281	59.00	23.80	16.59	17.11
70.00	0.477	59.00	23.80	28.16	12.44
80.00	0.610	59.00	23.80	36.00	9.28
90.00	0.779	59.00	23.80	45.95	5.26

GLUCOSE-WATER

WT% Glucose	XS Glucose	P_S^o Glucose	P_w^o H_2O	P_S Glucose	$P_w H_2O$
0.18	0.0002	0.00	23.80	0.00	23.80
0.89	0.0009	0.00	23.80	0.00	23.78
1.77	0.0018	0.00	23.80	0.00	23.76

TABLE II (CONT'D)

VAPOR PRESSURES OF PURE SOLVENTS; PARTIAL PRESSURES AND MOLE FRACTIONS OF VARIOUS AQUEOUS-ORGANIC MIXED SOLVENT MEDIA AT 35°C.

METHANOL-WATER

WT% MeOH	XS MeOH	P_S^o MeOH	P_w^o H_2O	P_S MeOH	P_w H_2O
10.00	0.059	187.70	42.20	11.04	39.72
20.00	0.123	187.70	42.20	23.14	37.00
30.00	0.194	187.70	42.20	36.46	34.00
50.00	0.360	187.70	42.20	67.57	27.01
70.00	0.568	187.70	42.20	106.53	18.25
80.00	0.692	187.70	42.20	129.94	12.99
90.00	0.836	187.70	42.20	156.74	6.96

ETHANOL-WATER

WT% EtOH	XS EtOH	P_S^o EtOH	P_w^o H_2O	P_S EtOH	P_w H_2O
10.00	0.042	103.70	42.20	4.32	40.44
20.00	0.089	103.70	42.20	9.24	38.44
30.00	0.144	103.70	42.20	14.89	36.14
50.00	0.281	103.70	42.20	29.16	30.33
70.00	0.477	103.70	42.20	49.49	22.06
80.00	0.610	103.70	42.20	63.27	16.45
90.00	0.779	103.70	42.20	80.76	9.33

GLUCOSE-WATER

WT% Glucose	XS Glucose	P_S^o Glucose	P_w^o H_2O	P_S Glucose	$P_w H_2O$
0.18	0.0002	0.00	42.20	0.00	42.19
0.89	0.0009	0.00	42.20	0.00	42.16
1.77	0.0018	0.00	42.20	0.00	42.12

TABLE II (CONT'D)

VAPOR PRESSURES OF PURE SOLVENTS; PARTIAL PRESSURES AND MOLE FRACTIONS OF VARIOUS AQUEOUS-ORGANIC MIXED SOLVENT MEDIA AT 40°C.

METHANOL-WATER

WT% MeOH	XS MeOH	P_s^o MeOH	P_w^o H_2O	P_s MeOH	P_w H_2O
10.00	0.059	237.15	55.30	13.95	52.05
20.00	0.123	237.15	55.30	29.23	48.48
30.00	0.194	237.15	55.30	46.06	44.56
50.00	0.360	237.15	55.30	85.37	35.39
70.00	0.568	237.15	55.30	134.59	23.91
80.00	0.692	237.15	55.30	164.18	17.02
90.00	0.835	237.15	55.30	198.03	9.12

ETHANOL-WATER

WT% EtOH	XS EtOH	P_s^o EtOH	P_w^o H_2O	P_s EtOH	P_w H_2O
10.00	0.042	135.30	55.30	5.64	53.00
20.00	0.089	135.30	55.30	12.05	50.37
30.00	0.144	135.30	55.30	19.43	47.36
50.00	0.281	135.30	55.30	38.05	39.75
70.00	0.477	135.30	55.30	64.57	28.91
80.00	0.610	135.30	55.30	82.55	21.56
90.00	0.779	135.30	55.30	105.37	12.23

GLUCOSE-WATER

WT% Glucose	XS Glucose	P_s^o Glucose	P_w^o H_2O	P_s Glucose	P_w H_2O
0.18	0.0002	0.00	55.30	0.00	55.29
0.89	0.0009	0.00	55.30	0.00	55.25
1.77	0.0018	0.00	55.30	0.00	55.20

$$[HA] = C_A - [H^+] \tag{63}$$

Substitution of equations (62) and (63) into equation (61) yields

$$K_i = \frac{[H^+]^2}{([HA] - [H^+])} \tag{64}$$

Since the hydrogen ion concentration had been computed in the form of the pH of each of the lactic acid test solutions, it was convenient to convert the above equation into one relating the pK_i of each particular solution to its pH. The relation between the pK_i's of the solutions and their respective pH's can be derived simply by taking the negative logarithm of equation (64):

$$-\log K_i = -\log ([H^+]^2 / ([HA] - [H^+])) \tag{65}$$

The above equation reduces to

$$pK_i = (-\log [H^+]^2) - (-\log ([HA] - [H^+])) \tag{66}$$

which can be further simplified to

$$pK_i = 2(-\log [H^+]) + \log ([HA] - [H^+]) \tag{67}$$

or, more concisely

$$pK_i = 2\ pH + \log ([HA] - [H^+]) \tag{68}$$

Recalling that $[H^+] = 10^{-pH}$, we can substitute into equation (68) to obtain

$$pK_i = 2\ pH + \log ([HA] - 10^{-pH}) \tag{69}$$

which was the final form that was employed in the computation of the pK_i^*'s of lactic acid at various temperatures in different mixed solvent media. These values of the pK_i^*'s are compiled in Tables IV and VI under the heading Experimental pK_i^*.

Sen and Adcock (93) have demonstrated for the case of monoprotic organic acids that the pK_i^*'s in mixed solvent media and the pK_i's in aqueous media are related by the equation

TABLE III

DIELECTRIC CONSTANTS OF VARIOUS AQUEOUS-ORGANIC MIXED SOLVENTS AT DIFFERENT TEMPERATURES (47)

ETHANOL-WATER

WT % SOLVENT	T = 15°C	T = 25°C	T = 35°C	T = 40°C
10	76.41	72.80	69.40	67.86
20	70.37	67.00	63.77	62.41
30	64.25	61.10	58.03	56.73
50	51.81	49.00	46.39	45.30
70	40.34	38.00	35.75	34.88
80	34.96	32.80	30.85	29.83
90	29.92	28.10	26.44	25.64

METHANOL-WATER

WT% SOLVENT	T = 15°C	T = 25°C	T = 35°C	T = 40°C
10	77.68	74.10	70.58	68.90
20	72.63	69.20	65.87	64.13
30	67.59	64.30	61.14	59.53
50	57.94	54.90	52.02	50.40
70	47.69	45.00	42.46	41.04
80	42.50	40.10	37.91	36.66
90	37.75	35.70	33.77	32.56

TABLE III (CONT'D)

DIELECTRIC CONSTANTS OF THE VARIOUS MIXED SOLVENT COMBINATIONS OF D-GLUCOSE AT SEVERAL DIFFERENT TEMPERATURES

GLUCOSE-WATER

WT % SOLVENT	T = 15°C	T = 25°C	T = 35°C	T = 40°C
1.77	81.77	78.12	74.59	72.88
0.89	82.00	78.33	74.80	73.08
0.18	82.17	78.50	74.96	73.24

Furth, Reinhold, Annalen der Physik, 22, 63-80 (1922)

TABLE IV

PK_1^*'s OF LACTIC ACID IN METHANOL-WATER MIXED SOLVENT MEDIA AT VARIOUS TEMPERATURES

WT % MeOH	MF MeOH	T = 15°C pK_1^*		T = 25°C pK_1^*		T = 35°C pK_1^*	
		Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
10.00	0.059	4.02	3.95	3.82	3.95	3.56	3.96
20.00	0.123	4.17	4.05	3.93	4.06	3.74	4.08
30.00	0.194	4.38	4.18	4.16	4.19	4.20	4.22
50.00	0.360	4.44	4.47	4.54	4.51	4.52	4.57
70.00	0.568	4.82	4.92	5.30	5.00	4.90	5.09
80.00	0.692	.1	5.22	5.24	5.32	5.39	5.43
90.00	0.835	5.52	5.58	5.52	5.69	5.86	5.82

WT % MeOH	MF MeOH	T = 40°C pK_1^*	
		Exptl	Calcd
10.00	0.059	3.19	3.97
20.00	0.123	3.58	3.97
30.00	0.194	3.83	4.25
50.00	0.360	3.97	4.61
70.00	0.568	4.12	5.16
80.00	0.692	4.73	5.50
90.00	0.835	5.52	5.92

TABLE V

pK_1^*'s OF LACTIC ACID IN ETHANOL-WATER MIXED SOLVENT MEDIA AT VARIOUS TEMPERATURES

WT % EtOH	MF EtOH	T = 15°C pK_1^*		T = 25°C pK_1^*		T = 35°C pK_1^*	
		Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.71	3.97	3.69	3.98	3.28	3.99
20.00	0.089	3.93	4.11	3.82	4.12	3.55	4.14
30.00	0.143	4.01	4.27	4.20	4.29	3.46	4.33
50.00	0.281	4.58	4.72	4.65	4.78	4.66	4.85
70.00	0.477	5.22	5.38	5.58	5.49	5.40	5.62
80.00	0.610	5.80	5.83	6.23	5.99	5.39	6.15
90.00	0.779	6.27	6.41	6.47	6.60	6.05	6.80

WT % EtOH	MF EtOH	T = 40°C pK_1^*	
		Exptl	Calcd
10.00	0.042	3.16	4.00
20.00	0.089	3.41	4.15
30.00	0.143	4.14	4.35
50.00	0.281	4.47	4.88
70.00	0.477	5.27	5.67
80.00	0.610	6.35	6.25
90.00	0.779	7.43	6.91

TABLE VI

PK_1^*'s OF LACTIC ACID IN GLUCOSE-WATER ,IXED SOLVENT MEDIA AT VARIOUS TEMPERATURES

WT% Glucose	MF Glucose	T = 15°C pK_1^*		T = 25°C pK_1^*		T = 35°C pK_1^*	
		Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	3.91	3.90	3.67	3.90	3.47	3.91
0.0089	0.0009	3.74	3.88	3.47	3.88	3.48	3.89
0.0177	0.0018	3.98	3.86	3.88	3.86	3.83	3.86

WT % Glucose	MF Glucose	T = 40°C pK_1^*	
		Exptl	Calcd
0.0018	0.0002	3.37	3.92
0.0089	0.0009	3.68	3.90
0.0177	0.0018	3.77	3.87

$$pK_i^* = pK_i + \beta(1/\varepsilon^* - 1/\varepsilon) \quad (70)$$

where pK_i^* equals the negative logarithm of the ionization constant of the acid in the mixed solvent, pK_i equals the negative logarithm of the ionization constant in water, ε^* is the bulk dielectric constant of the mixed solvent, and is the dielectric constant of water. Sen and Adcock (93) found that the average value of the empirical constant β, as determined from a study of thirteen monoprotic acids in six different mixed solvents, was 120. This is the value of β that we have used in equation (70) in computing the calculated values of pK_i^*, which were reported in Table IV to VI. The pK_i values were computed from the temperature-dependence equation formulated by Martin and Tartar (73) on the basis of their conductance measurements:

$$pK_i = 3.857 + 5.00 \times 10^{-5} (t = 22.5)^2 \quad (71)$$

where t is the desired temperature in ^{o}C. This equation is identical in form to the one suggested by Harned and Embree (52) for the generalized case of all monoprotic weak acids.

Dielectric constant data for methanol and ethanol were provided by Akerlof (31), and those for glucose were obtained from Furth (48). Table III summarizes the dielectric constants of each of the three pure solvents and their various combinations at each of the temperature values that were investigated.

Equations (70) and (71) provided us with a means of calculating pK_i^* and testing the goodness of our experimental pK_i^* and also of checking the validity of Sen and Adcock's equation. The data for the calculation of the experimental pK_i^*'s were obtained from potentiometric measurements of cells of the same type as Cell V containing lactic acid of five different concentrations (0.2 molal, 0.1 molal, 0.05 molal, 0.01

molal, and 0.005 molal). The pK_i^* values for each of the five concentrations were calculated, and the highest and lowest values were rejected; the remaining three were averaged to yield the experimental pK_i^*'s that are listed in Tables IV to VI.

We made the preliminary assumption that the formation constant of a metal complex in a mixed solvent medium, and the formation constant of the same complex in water, might be related by an equation similar in form to that of Sen and Adcock for acids. Consider the equilibrium

$$M + L \rightleftharpoons ML$$

where the formation constant is given by

$$K_f = \frac{[ML]}{[M][L]} = 1/K_{inst} \tag{72}$$

in which K_{inst} is the instability constant of the complex. Therefore, the ionization constant K_i of an acid and the instability constant K_{inst} of a complex are expressed by analogous algebraic forms. It follows that

$$-\log K_{inst} = pK_{inst} = \log K_f \tag{73}$$

The equation that we have chosen to test should be of the general form

$$\log K_{av}^* = \log K_{av} + \beta(1/\varepsilon^* - 1/\varepsilon) \tag{74}$$

It is interesting to note an equation of the same form as equation (74) can be derived using Born's electrostatic model (8). The physical process of ionization is visualized as the separation of two particles, charging them and removing them to an infinite distance of separation. The starting point of the calculation according to Born's model is to calculate the electrical work involved in charging a sphere of radius a in a uniform dielectric medium. It can be shown (8) from electrostatics that the work involved in charging a sphere of radium a placed in a homogeneous dielectric medium is given by

$$W = \frac{q^2}{2\epsilon a} \tag{75}$$

where q is the charge and ϵ is the dielectric constant of the medium. If we now make the assumption that the central metal ion can be treated as a sphere with a fixed radius (valid for the spherically symmetrical d^0, d^5, and d^{10} metal ions that were investigated) and also that the dielectric constant of the solvent is uniform, then our calculations for the work involved in the charging of the sphere can be equated to the free energy of the ion with respect to the uncharged species in the same given solvent.

In applying the Born equation to problems involving formation constants, we will express the work of charging an ion in the more general form

$$W = \frac{1}{\epsilon} \frac{z_i^2 e^2}{2r_i} \tag{76}$$

where z_i is the number of unit charges on the ion i and e is the electronic charge. If the same form of the equation holds for both the positive and the negative ions, the total work for N ions of each type will be

$$W_+ + W_- = \frac{N\nu_+ z_+^2 e^2}{2r_+\epsilon} \quad \frac{N\nu_- z_-^2 e^2}{2r_-\epsilon} \tag{77}$$

where ν_+ is the number of positive ions produced when one molecule undergoes ionization, ν_- is the number of negative ion per molecule formed through molecular dissociation, and r is the average ionic radius of the two ion types. In determining formation constants, we are interested in the relative stability of a metallic complex in one solvent with respect to another solvent. Thus, we must compute the work necessary to charge one of the ions of a given complex (whether it be the central metal ion or one of the ligands) in solvent 1 with

respect to the work necessary in another solvent, solvent 2. This relationship can be expressed as

$$W_{total} = (W_+ + W_-)_1 - (W_+ + W_-)_2 \tag{79}$$

Substitution of the results of equation (78) for each respective case yields

$$W_{total} = \frac{N_e^2}{2r_1\varepsilon_1}\left(v_+z_+^2 + v_-z_-^2\right) - \frac{Ne^2}{2r_2\varepsilon_2}\left(v_+z_+^2\right) \tag{80}$$

which reduces to

$$W_{total} = \frac{Ne^2}{2r}\left(v_+z_+^2 + v_-z_-^2\right)\left(1/\varepsilon_1 - 1/\varepsilon_2\right) \tag{81}$$

where r is the average ionic radius of the given electrolyte in solvents 1 and 2.

The final step in the development of the Born equation as it applies to equilibrium relationships concerning coordination complexes involves equating the energy of transfer of the ions from solvent 1 to solvent 2, to the ideal relation between the free energy and the solute concentration; that is

$$\Delta G = \Delta G^0 + RT \ln K \tag{82}$$

If the same standard reference state is used in both solvents, we can further say that

$$\Delta G_1 - \Delta G_2 = RT \ln K_1 - RT \ln K_2 \tag{83}$$

Now, by equating the work of transporting the electrolyte, W_{total}, to equation (83) and recognizing that there will be formed v_+ positive ions and v_- negative ions from the ionization of the electrolyte, we can see

$$\frac{Ne^2}{2r}\left(v_+z_+^2 + v_-z_-^2\right)\left(1/\varepsilon_1 - 1/\varepsilon_2\right) = RT \ln \frac{(v_+K_1)^{v+}(v_-K_1)^{v-}}{(v_+K_2)^{v+}(v_-K_2)^{v-}} \tag{84}$$

We can further reduce this equation by noting that, due to the symmetry of z with respect to v,

$$(v_+z_+^2 + v_-z_-^2) = z_+z_-(v_+ + v_-) \tag{85}$$

This fact can be coupled with the rearrangement of the right side of equation (84) due to the logarithmic relationship

$$RT \ln \frac{(v_+K_1)^{v+}(v_-K_1)^{v-}}{(v_+K_2)^{v+}(v_-K_2)^{v-}} = RT(v_+ + v_-) \ln \frac{K_1}{K_2} \tag{86}$$

to give upon division of both sides of equation (84) by $RT(v_+ + v_-)$ the final form of the Born equation

$$\ln K_1 = \ln K_2 + \frac{Ne^2}{2RT_r} z_+z_- (1/\varepsilon_1 - 1/\varepsilon_2) \tag{87}$$

which is identical in form and content to equation (74) if we consider that K_1 in this case equals our K^*_{av}, K_2 is equivalent to K_{av}, the term $\frac{Ne^2}{2RT_r} z_+z_-$ is the same as our constant β (positive, as predicted, in spite of the z_+z_- product term), and ε_1 and ε_2 correspond to ε^* and ε, respectively.

Thus, we can see that equation (74) is not just arbitrarily derived or empirically justified, but has sound theoretical basis as well. In the succeeding paragraphs, examples will be given to illustrate the case of the zinc complex of lactic acid specifically and the overall method employed in determining the various formation constants and intermediate quantities in general.

Since all titrimetric calculations involved in determining the values of $\log K_1$ and $\log K_2$ are similar, only one case of the complexation of the zinc ion is being described below in detail as an example.

The method outlined on page 21 for the determination of $\bar{n}$ requires titrations of two solutions of the ligand, one of them containing the metal ion and the other without. Detailed compositions of the two test solutions have been described in the Experimental section (Chapter III). During these titrations, the pH was followed with a standard hydrogen

electrode coupled with a Saturated Calomel Electrode. The apparatus used is depicted in Figure 2.

Figures 4 and 5 represent typical titration curves of the test solutions without the metal ion (Figure 4) and with the metal ion (Figure 5). Figure 6 represents a plot of $\bar{n}$ versus pC_A, from which log K_1 and log K_2 can be interpolated. The value of pC_A at $\bar{n} = 0.5$ corresponds to log K_1 and the value of pC_A at $\bar{n} = 1.5$ corresponds to log K_2. Figure 7 represents a plot of log K^*_{av} ($K^*_{av} = \sqrt{K_1 \cdot K_2}$) against $\sqrt{\mu}$, which denotes the value of log K^*_{av} at infinite dilution (extrapolated to zero ionic strength).

Although $\bar{n}$ is independent of volume, C_A is not. The latter is related to the concentration of the unbound ligand (S) by equation (v), on page 18, which depends on volume. The general formula used to calculate S is

$$S = \frac{0.400 - \Delta V(ml) \times 10^{-1}}{V_T} = \text{Total reagent - bound reagent (moles/l)}$$

where 0.400 = total reagent (lactic acid) in milliequivalents, ΔV = the difference in ml titrant between the curves in Figure 4 and Figure 5 at a given pH. When ΔV is multiplied by the normality of the titrant (10^{-1}), it gives the number of milliequivalents of bound reagent (ligand). V_T = total volume in ml of titrant. $\bar{n} = \frac{\text{concentration of bound ligand}}{\text{total concentration of metal}} = \frac{\Delta V \times 10^{-1}}{(2.5)(2.0 \times 10^{-2})}$ where the 5.0×10^{-2} milliequivalents of metal ion in the denominator arise from 2.5 ml of 2.0×10^{-2} M metal stock solution.

FIGURE 4:

TITRATION CURVE OF LACTIC ACID IN 30 PERCENT ETHANOL-WATER AT 25 °C. (μ = 0.050)

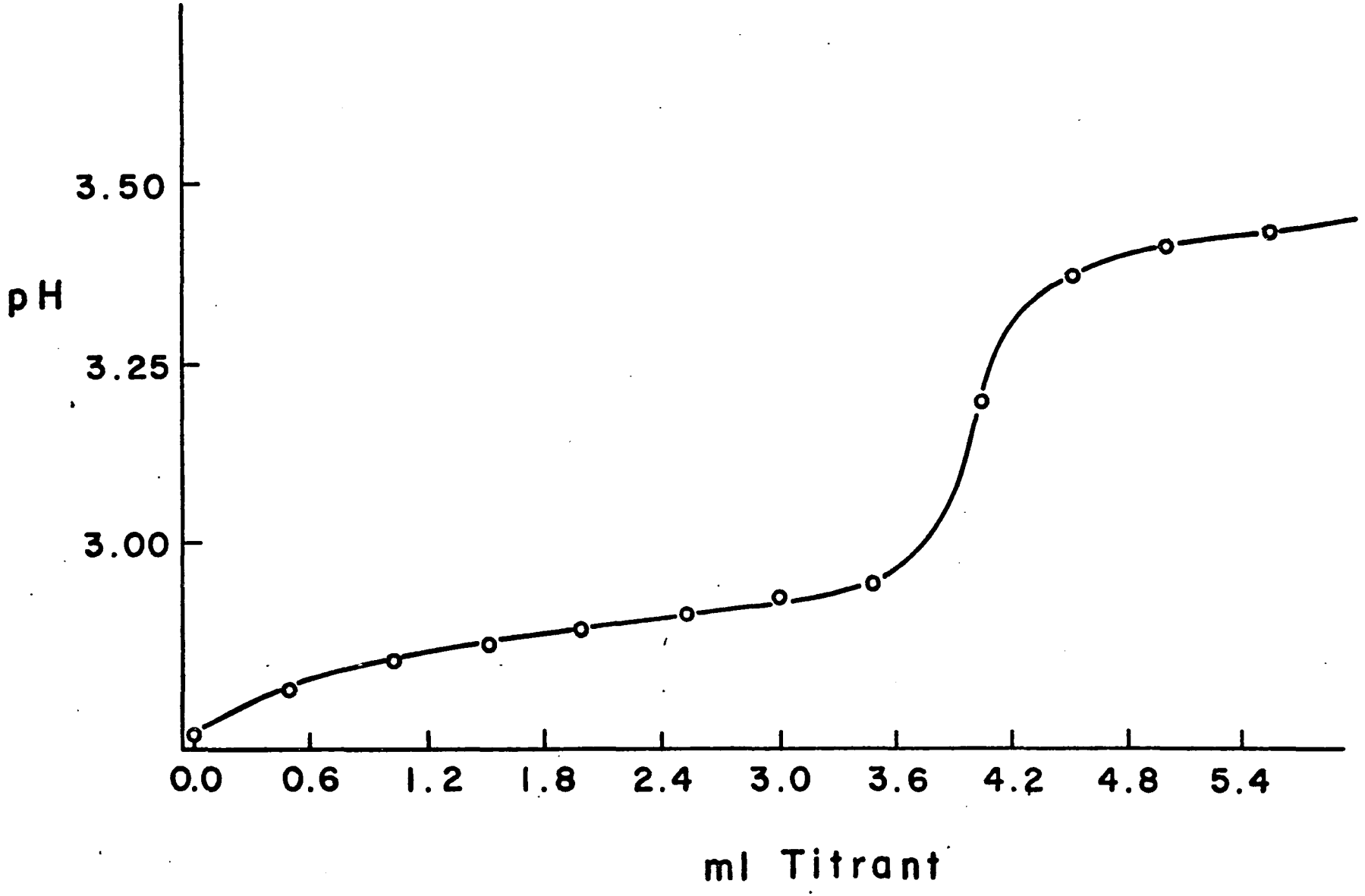

3.50
pH
3.25
3.00
0.0
0.6
1.2
1.8
2.4
3.0
3.6
4.2
4.8
5.4
ml Titrant

FIGURE 5:

TITRATION CURVE OF ZINC ION-LACTIC ACID SYSTEM IN 30 PERCENT ETHANOL-WATER AT 25° C (μ=0.050)

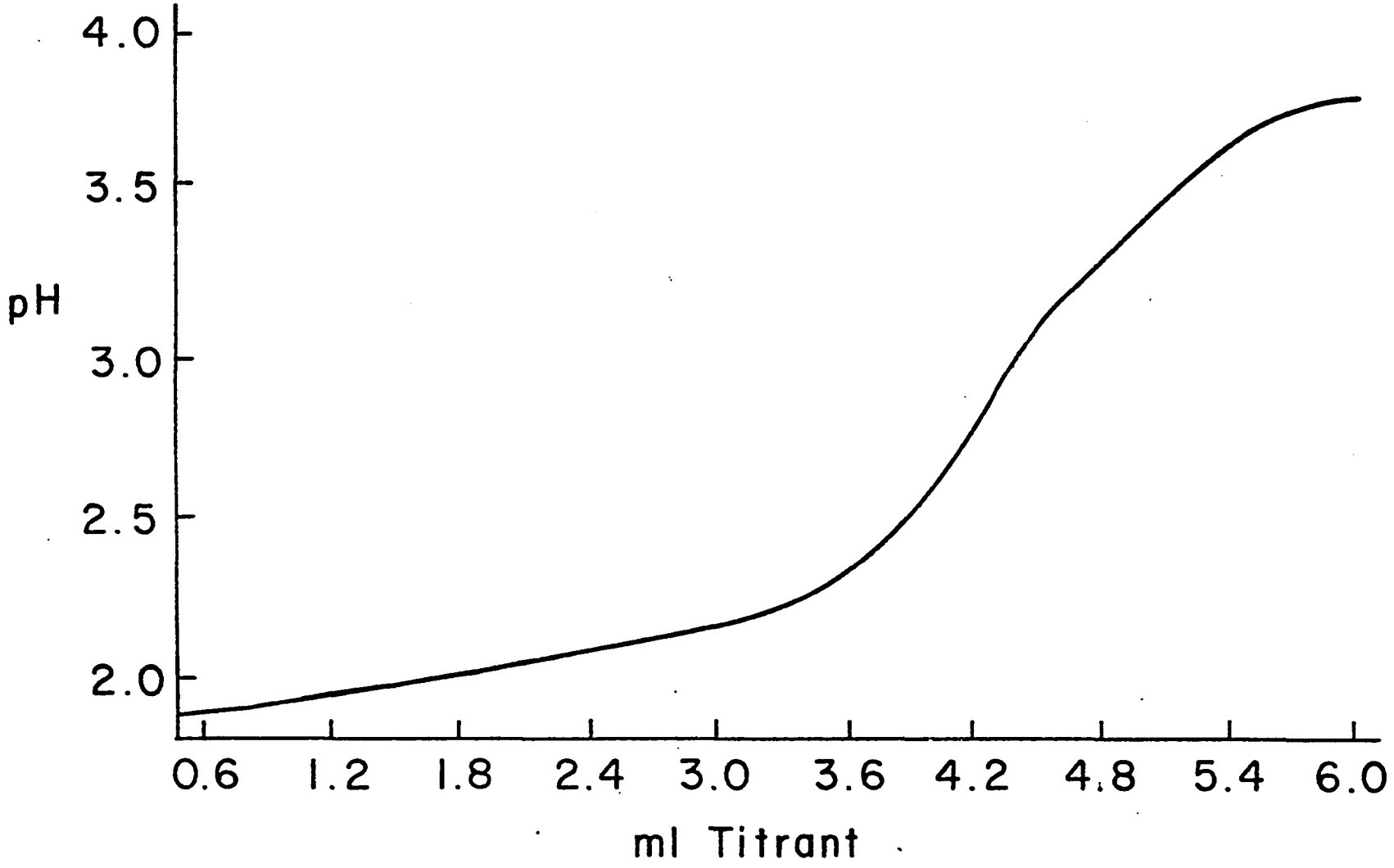

4.0
3.5
pH
3.0
2.5
2.0
0.6
1.2
1.8
2.4
3.0
3.6
4.2
4.8
5.4
6.0
ml Titrant

FIGURE 6

PLOT OF pC_A VERSUS $\bar{n}$ FOR ZINC ION-LACTIC ACID SYSTEM IN 30 PERCENT ETHANOL-WATER AT 25° C (μ=0.050)

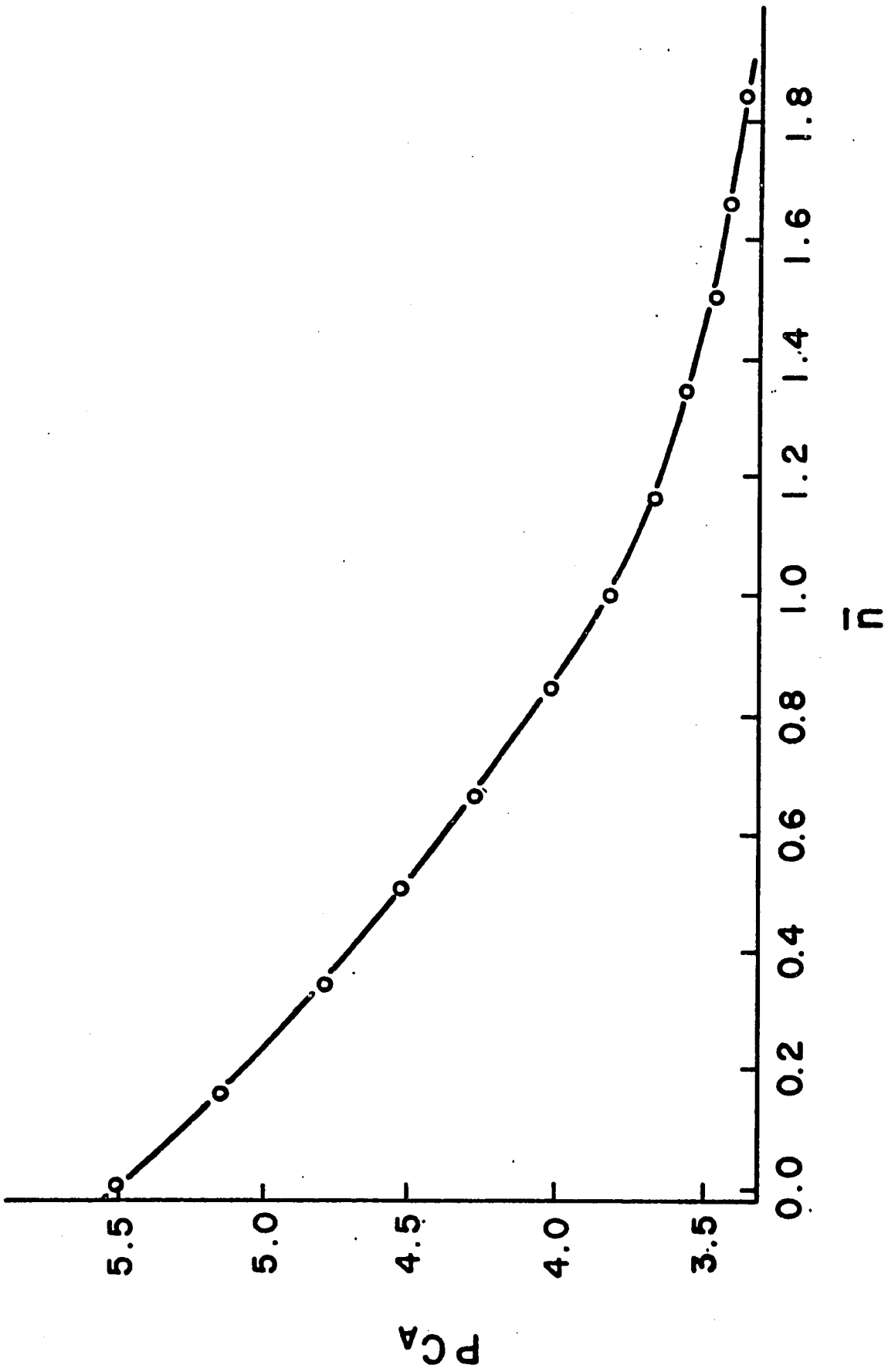

pCa
5.5
5.0
4.5
4.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
n̄

FIGURE 7:

PLOT OF LOG K_{av}^{*} VERSUS $\sqrt{\mu}$ FOR ZINC ION-LACTIC ACID SYSTEM IN 30 PERCENT ETHANOL-WATER AT 25° C (μ=0.050)

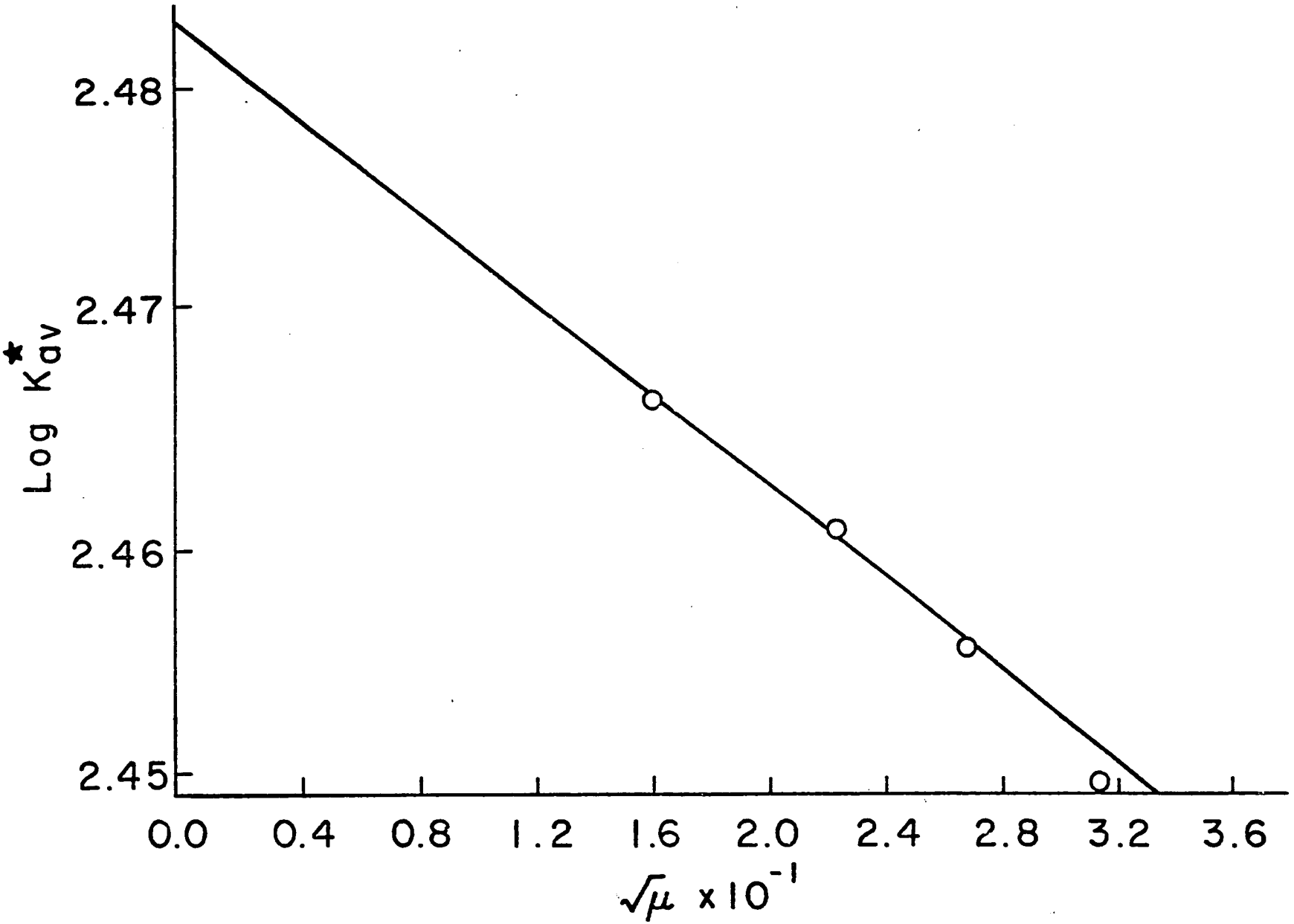

2.48
2.47
2.46
2.45
Log K*av
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
√μ x10⁻¹

TABLE VII

FIRST FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.44	1.59	1.58	3.9×10^1	3.8×10^1
20.00	0.123	1.44	1.78	1.75	6.0×10^1	5.6×10^1
30.00	0.194	1.44	2.00	1.94	1.0×10^2	8.8×10^1
50.00	0.360	1.44	2.51	2.41	3.3×10^2	2.6×10^2
70.00	0.568	1.44	3.29	3.12	2.0×10^3	1.3×10^3
80.00	0.692	1.44	3.83	3.60	6.7×10^3	4.0×10^3
90.00	0.835	1.44	4.45	4.16	2.8×10^4	1.5×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.44	1.64	1.62	4.3×10^1	4.1×10^1
20.00	0.089	1.44	1.87	1.83	7.5×10^1	6.8×10^1
30.00	0.144	1.44	2.16	2.09	1.4×10^2	1.2×10^2
50.00	0.281	1.44	2.94	2.80	8.7×10^3	6.3×10^3
70.00	0.477	1.44	4.09	3.84	1.2×10^4	6.9×10^3
80.00	0.610	1.44	4.89	4.57	7.8×10^4	3.7×10^4
90.00	0.779	1.44	5.91	5.48	8.1×10^5	3.0×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.44	1.442	1.442	2.77×10^1	2.76×10^1
0.89	0.0009	1.44	1.447	1.446	2.80×10^1	2.80×10^1
1.77	0.0018	1.44	1.454	1.453	2.85×10^1	2.84×10^1

TABLE VIII

FIRST FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.56	1.72	1.70	5.2×10^1	5.1×10^1
20.00	0.123	1.56	1.92	1.89	8.3×10^1	7.7×10^1
30.00	0.194	1.56	2.15	2.09	1.4×10^2	1.2×10^2
50.00	0.360	1.56	2.71	2.60	5.1×10^2	4.0×10^2
70.00	0.568	1.56	3.55	3.36	3.6×10^3	2.3×10^3
80.00	0.692	1.56	4.12	3.88	1.3×10^4	7.5×10^3
90.00	0.835	1.56	4.77	4.46	5.8×10^4	2.9×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.56	1.77	1.75	5.9×10^1	5.6×10^1
20.00	0.089	1.56	2.02	1.98	1.0×10^2	9.4×10^1
30.00	0.144	1.56	2.32	2.25	2.1×10^2	1.8×10^2
50.00	0.281	1.56	3.17	3.02	1.5×10^3	1.0×10^3
70.00	0.477	1.56	4.41	4.14	2.6×10^4	1.4×10^4
80.00	0.610	1.56	5.29	4.93	1.9×10^5	8.6×10^4
90.00	0.779	1.56	6.36	5.90	2.3×10^6	8.0×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.56	1.561	1.561	3.64×10^1	3.64×10^1
0.89	0.0009	1.56	1.567	1.566	3.69×10^1	3.69×10^1
1.77	0.0018	1.56	1.574	1.573	3.75×10^1	3.74×10^1

TABLE IX

FIRST FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.76	1.93	1.91	8.5×10^1	8.2×10^1
20.00	0.123	1.76	2.14	2.11	1.4×10^2	1.3×10^2
30.00	0.194	1.76	2.39	2.33	2.5×10^2	2.1×10^2
50.00	0.360	1.76	2.99	2.88	9.8×10^2	7.5×10^2
70.00	0.568	1.76	3.90	3.70	8.0×10^3	5.0×10^3
80.00	0.692	1.76	4.49	4.23	3.1×10^4	1.7×10^4
90.00	0.835	1.76	5.17	4.85	1.5×10^5	7.1×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.76	1.98	1.96	8.5×10^1	8.2×10^1
20.00	0.089	1.76	2.25	2.20	1.8×10^2	1.6×10^2
30.00	0.144	1.76	2.57	2.50	3.8×10^2	3.1×10^2
50.00	0.281	1.76	3.48	3.32	3.0×10^3	2.1×10^3
70.00	0.477	1.76	4.83	4.54	6.8×10^4	3.4×10^4
80.00	0.610	1.76	5.76	5.38	5.8×10^5	2.4×10^5
90.00	0.779	1.76	6.90	6.41	7.9×10^6	2.6×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.76	1.763	1.763	5.79×10^1	5.79×10^1
0.89	0.0009	1.76	1.769	1.768	5.87×10^1	5.86×10^1
1.77	0.0018	1.76	1.777	1.775	5.98×10^1	5.96×10^1

TABLE X

FIRST FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.94	2.12	2.19	1.3×10^2	1.3×10^2
20.00	0.123	1.94	2.34	2.30	2.2×10^2	2.0×10^2
30.00	0.194	1.94	2.60	2.53	3.9×10^2	3.4×10^2
50.00	0.360	1.94	3.23	3.11	1.7×10^3	1.3×10^3
70.00	0.568	1.94	4.18	3.97	1.5×10^4	9.4×10^3
80.00	0.692	1.94	4.80	4.52	6.3×10^4	3.3×10^4
90.00	0.835	1.94	5.52	5.18	3.3×10^5	1.5×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.94	2.16	2.14	1.5×10^2	1.4×10^2
20.00	0.089	1.94	2.43	2.39	2.7×10^2	2.4×10^2
30.00	0.144	1.94	2.77	2.69	5.9×10^2	4.9×10^2
50.00	0.281	1.94	3.70	3.54	5.1×10^3	3.4×10^3
70.00	0.477	1.94	5.09	4.79	1.2×10^5	6.1×10^4
80.00	0.610	1.94	6.11	5.71	1.3×10^6	5.1×10^5
90.00	0.779	1.94	7.26	6.75	1.8×10^7	5.6×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.94	1.944	1.944	8.8×10^1	8.8×10^1
0.89	0.0009	1.94	1.951	1.950	8.9×10^1	8.9×10^1
1.77	0.0018	1.94	1.958	1.957	9.1×10^1	9.1×10^1

TABLE XI

SECOND FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.02	1.17	1.16	1.5×10^1	1.4×10^1
20.00	0.123	1.02	1.36	1.33	2.3×10^1	2.1×10^1
30.00	0.194	1.02	1.58	1.52	3.8×10^1	3.3×10^1
50.00	0.360	1.02	2.09	1.99	1.2×10^2	9.8×10^1
70.00	0.692	1.02	2.87	2.70	7.4×10^2	1.5×10^3
80.00	0.692	1.02	3.41	3.18	2.6×10^3	1.5×10^3
90.00	0.835	1.02	4.03	3.74	1.1×10^4	5.5×10^3

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.02	1.22	1.20	1.6×10^1	1.6×10^1
20.00	0.089	1.02	1.45	1.41	2.8×10^1	2.6×10^1
30.00	0.144	1.02	1.74	1.67	5.5×10^1	4.7×10^1
50.00	0.281	1.02	2.52	2.38	3.3×10^2	2.4×10^2
70.00	0.477	1.02	3.67	3.42	4.7×10^3	2.6×10^3
80.00	0.610	1.02	4.47	4.15	3.0×10^4	1.4×10^4
90.00	0.779	1.02	5.49	5.06	3.1×10^5	1.2×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.02	1.022	1.022	1.05×10^1	1.05×10^1
0.89	0.0009	1.02	1.027	1.026	1.06×10^1	1.06×10^1
1.77	0.0018	1.02	1.034	1.033	1.08×10^1	1.08×10^1

TABLE XII

SECOND FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.14	1.30	1.28	2.0×10^1	1.9×10^1
20.00	0.123	1.14	1.50	1.47	3.2×10^1	2.9×10^1
30.00	0.194	1.14	1.73	1.67	5.4×10^1	4.7×10^1
50.00	0.360	1.14	2.29	2.18	1.9×10^2	1.5×10^2
70.00	0.568	1.14	3.13	2.94	1.4×10^3	8.7×10^2
80.00	0.692	1.14	3.70	3.46	5.0×10^3	2.9×10^3
90.00	0.835	1.14	4.35	4.04	2.2×10^4	1.1×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.14	1.35	1.33	2.2×10^1	2.1×10^1
20.00	0.089	1.14	1.60	1.56	4.0×10^1	3.6×10^1
30.00	0.144	1.14	1.90	1.83	8.0×10^1	6.7×10^1
50.00	0.281	1.14	2.75	2.60	5.6×10^2	4.0×10^2
70.00	0.477	1.14	3.99	3.72	9.8×10^3	5.2×10^3
80.00	0.610	1.14	4.87	4.51	7.4×10^4	3.3×10^4
90.00	0.779	1.14	5.94	5.48	8.7×10^5	3.0×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.14	1.141	1.141	1.38×10^1	1.38×10^1
0.89	0.0009	1.14	1.147	1.146	1.40×10^1	1.40×10^1
1.77	0.0018	1.14	1.154	1.153	1.43×10^1	1.42×10^1

TABLE XIII

SECOND FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.26	1.43	1.41	2.7×10^1	2.6×10^1
20.00	0.123	1.26	1.64	1.61	4.4×10^1	4.0×10^1
30.00	0.194	1.26	1.89	1.83	7.8×10^1	6.8×10^1
50.00	0.360	1.26	2.49	2.38	3.1×10^2	2.4×10^2
70.00	0.568	1.26	3.40	3.20	2.5×10^3	1.6×10^3
80.00	0.692	1.26	3.99	3,73	9.9×10^3	5.4×10^3
90.00	0.835	1.26	4.67	4.35	4.7×10^4	2.2×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.26	1.48	1.46	3.0×10^1	2.9×10^1
20.00	0.089	1.26	1.75	1.70	5.6×10^1	5.0×10^1
30.00	0.144	1.26	2.07	2.00	1.2×10^2	1.0×10^2
50.00	0.281	1.26	2.98	2.82	9.6×10^2	6.6×10^2
70.00	0.477	1.26	4.33	4.04	2.1×10^4	1.1×10^4
80.00	0.610	1.26	5.26	4.88	1.8×10^5	7.6×10^4
90.00	0.779	1.26	6.40	5.91	2.5×10^6	8.1×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.26	1.263	1.263	1.83×10^1	1.83×10^1
0.89	0.0009	1.26	1.269	1.268	1.86×10^1	1.85×10^1
1.77	0.0018	1.26	1.277	1.275	1.89×10^1	1.88×10^1

TABLE XIV

SECOND FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.45	1.63	1.61	4.2×10^1	4.1×10^1
20.00	0.123	1.45	1.85	1.81	7.1×10^1	6.5×10^1
30.00	0.194	1.45	2.11	2.04	1.3×10^2	1.1×10^2
50.00	0.360	1.45	2.74	2.62	5.6×10^2	4.2×10^2
70.00	0.568	1.45	3.69	3.48	5.0×10^3	3.0×10^3
80.00	0.692	1.45	4.31	4.02	2.0×10^4	1.1×10^4
90.00	0.835	1.45	5.03	4.69	1.1×10^5	4.9×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.45	1.67	1.65	4.7×10^1	4.5×10^1
20.00	0.089	1.45	1.94	1.90	8.8×10^1	7.9×10^1
30.00	0.144	1.45	2.28	2.20	1.9×10^2	1.6×10^2
50.00	0.281	1.45	3.21	3.05	1.6×10^3	1.1×10^3
70.00	0.477	1.45	4.60	4.30	4.0×10^4	2.0×10^4
80.00	0.610	1.45	5.62	5.22	4.1×10^5	1.7×10^5
90.00	0.779	1.45	6.77	6.26	6.77×10^6	1.8×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.45	1.454	1.454	2.85×10^1	2.84×10^1
0.89	0.0009	1.45	1.461	1.460	2.89×10^1	2.88×10^1
1.77	0.0018	1.45	1.468	1.467	2.94×10^1	2.93×10^1

TABLE XV

FIRST FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.83	3.98	4.01	9.6×10^3	1.0×10^4
20.00	0.123	3.83	4.17	4.23	1.5×10^4	1.7×10^4
30.00	0.194	3.83	4.38	4.49	2.4×10^4	3.1×10^4
50.00	0.360	3.83	4.90	5.11	8.0×10^4	1.3×10^5
70.00	0.568	3.83	5.68	6.03	4.8×10^5	1.1×10^6
80.00	0.692	3.83	6.22	6.67	1.7×10^6	4.7×10^6
90.00	0.835	3.83	6.84	7.41	6.9×10^6	2.6×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.83	4.03	4.06	1.1×10^4	1.2×10^4
20.00	0.089	3.83	4.26	4.34	1.8×10^4	2.2×10^4
30.00	0.144	3.83	4.55	4.68	3.5×10^4	4.8×10^4
50.00	0.281	3.83	5.33	5.62	2.1×10^5	4.1×10^4
70.00	0.477	3.83	6.48	6.99	3.0×10^6	9.8×10^6
80.00	0.610	3.83	7.28	7.94	1.9×10^7	8.8×10^7
90.00	0.779	3.38	8.30	9.15	2.0×10^8	1.4×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.83	3.832	3.832	6.79×10^3	6.80×10^3
0.89	0.0009	3.83	3.837	3.839	6.87×10^3	6.89×10^3
1.77	0.0018	3.83	3.844	3.847	6.99×10^3	7.03×10^3

TABLE XVI

FIRST FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.64	3.80	3.83	6.3×10^3	6.7×10^3
20.00	0.123	3.64	4.00	4.07	1.0×10^4	1.2×10^4
30.00	0.194	3.64	4.23	4.34	1.7×10^4	2.2×10^4
50.00	0.360	3.64	4.79	5.01	6.2×10^4	1.0×10^5
70.00	0.568	3.64	5.63	6.01	4.3×10^5	1.0×10^6
80.00	0.692	3.64	6.20	6.69	1.6×10^6	4.9×10^6
90.00	0.835	3.64	6.85	7.46	7.0×10^6	2.9×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.64	3.85	3.89	7.1×10^3	7.8×10^3
20.00	0.089	3.64	4.10	4.19	1.3×10^4	1.5×10^4
30.00	0.144	3.64	4.40	4.55	2.5×10^4	3.5×10^4
50.00	0.281	3.64	5.25	5.56	1.8×10^5	3.6×10^5
70.00	0.477	3.64	6.49	7.03	3.1×10^6	1.1×10^7
80.00	0.610	3.64	7.37	8.08	2.3×10^7	1.2×10^8
90.00	0.779	3.64	8.44	9.35	2.7×10^8	2.2×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.64	3.641	3.642	4.38×10^3	4.38×10^3
0.89	0.0009	3.64	3.647	3.649	4.44×10^3	4.45×10^3
1.77	0.0018	3.64	3.654	3.657	4.51×10^3	4.54×10^3

TABLE XVII

FIRST FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.52	3.69	3.72	4.9×10^3	5.3×10^3
20.00	0.123	3.52	3.90	3.98	8.0×10^3	9.5×10^3
30.00	0.194	3.52	4.15	4.27	1.4×10^4	1.9×10^4
50.00	0.360	3.52	4.75	4.99	5.6×10^4	9.7×10^4
70.00	0.568	3.52	5.66	6.07	4.6×10^5	1.2×10^5
80.00	0.692	3.52	6.25	6.78	1.8×10^6	6.0×10^6
90.00	0.835	3.52	6.93	7.58	8.6×10^6	3.8×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.52	3.74	3.78	5.5×10^3	6.1×10^3
20.00	0.089	3.52	4.01	4.10	1.0×10^4	1.3×10^4
30.00	0.144	3.52	4.33	4.49	2.2×10^4	3.1×10^4
50.00	0.281	3.52	5.24	5.57	1.7×10^5	3.7×10^5
70.00	0.477	3.52	6.59	7.17	3.9×10^6	1.5×10^7
80.00	0.610	3.52	7.52	8.28	3.3×10^7	1.9×10^8
90.00	0.779	3.52	8.66	9.64	4.6×10^8	4.3×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.52	3.523	3.524	3.33×10^3	3.34×10^3
0.89	0.0009	3.52	3.529	3.531	3.38×10^3	3.39×10^3
1.77	0.0018	3.52	3.537	3.540	3.44×10^3	3.47×10^3

TABLE XVIII

FIRST FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.40	3.58	3.61	3.8×10^3	4.1×10^3
20.00	0.123	3.40	3.80	3.88	6.3×10^3	7.6×10^3
30.00	0.194	3.40	4.06	4.18	1.1×10^4	1.5×10^4
50.00	0.368	3.40	4.69	4.94	5.0×10^4	8.7×10^4
70.00	0.568	3.40	5.64	6.07	4.4×10^5	1.2×10^5
80.00	0.692	3.40	6.26	6.80	1.8×10^6	6.3×10^6
90.00	0.835	3.40	6.98	7.66	9.5×10^6	4.6×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.40	3.62	3.66	4.2×10^3	4.6×10^3
20.00	0.089	3.40	3.89	3.99	7.8×10^3	9.7×10^3
30.00	0.144	3.40	4.23	4.39	1.7×10^4	2.4×10^4
50.00	0.281	3.40	5.16	5.50	1.5×10^5	3.2×10^5
70.00	0.477	3.40	6.55	7.15	3.5×10^6	1.4×10^7
80.00	0.610	3.40	7.57	8.36	3.7×10^7	2.3×10^8
90.00	0.779	3.40	8.72	9.73	5.2×10^8	5.4×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.40	3.404	3.405	2.54×10^3	2.54×10^3
0.89	0.0009	3.40	3.411	3.413	2.57×10^3	2.59×10^3
1.77	0.0018	3.40	3.418	3.422	2.62×10^3	2.64×10^3

TABLE XIX

SECOND FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	4.01	4.16	4.19	1.4×10^4	1.5×10^4
20.00	0.123	4.01	4.35	4.41	2.2×10^4	2.5×10^4
30.00	0.194	4.01	4.56	4.67	3.7×10^4	4.7×10^4
50.00	0.360	4.01	5.08	5.28	1.2×10^5	1.9×10^5
70.00	0.568	4.01	5.86	6.21	7.3×10^5	1.6×10^6
80.00	0.692	4.01	6.40	6.85	2.5×10^6	7.2×10^6
90.00	0.835	4.01	7.02	7.59	1.0×10^7	3.9×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	4.01	4.21	4.24	1.6×10^4	1.5×10^4
20.00	0.089	4.01	4.44	4.52	2.8×10^4	3.3×10^4
30.00	0.144	4.01	4.73	4.86	5.3×10^4	7.3×10^4
50.00	0.281	4.01	5.51	5.90	3.2×10^5	6.3×10^5
70.00	0.477	4.01	6.66	7.17	4.6×10^6	1.5×10^7
80.00	0.610	4.01	7.46	8.12	2.9×10^7	1.3×10^8
90.00	0.779	4.01	8.48	9.33	3.0×10^8	2.1×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	4.01	4.012	4.012	1.03×10^4	1.03×10^4
0.89	0.0009	4.01	4.017	4.018	1.04×10^4	1.04×10^4
1.77	0.0018	4.01	4.024	4.027	1.06×10^4	1.07×10^4

TABLE XX

SECOND FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.82	3.98	4.01	9.5×10^3	1.0×10^4
20.00	0.123	3.82	4.18	4.25	1.5×10^4	1.8×10^4
30.00	0.194	3.82	4.41	4.52	2.6×10^4	3.3×10^4
50.00	0.360	3.82	4.97	5.19	9.3×10^4	1.6×10^5
70.00	0.568	3.82	5.81	6.19	6.5×10^5	1.6×10^6
80.00	0.692	3.82	6.38	6.87	2.4×10^6	7.4×10^6
90.00	0.835	3.82	7.03	7.64	1.1×10^7	4.3×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.82	4.03	4.07	1.1×10^4	1.2×10^4
20.00	0.089	3.82	4.28	4.37	1.9×10^4	2.3×10^4
30.00	0.144	3.82	4.58	4.73	3.8×10^4	5.3×10^4
50.00	0.281	3.82	5.43	5.74	2.7×10^5	5.4×10^4
70.00	0.477	3.82	6.67	7.21	4.7×10^6	1.6×10^7
80.00	0.610	3.82	7.55	8.26	3.5×10^7	1.8×10^8
90.00	0.779	3.82	8.62	9.53	4.2×10^8	3.4×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.82	3.821	3.822	6.63×10^3	6.63×10^3
0.89	0.0009	3.82	3.827	3.829	6.72×10^3	6.74×10^3
1.77	0.0018	3.82	3.834	3.837	6.83×10^3	6.87×10^3

TABLE XXI

SECOND FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.70	3.87	3.90	7.4×10^3	8.0×10^3
20.00	0.123	3.70	4.08	4.16	1.2×10^4	1.4×10^4
30.00	0.194	3.70	4.33	4.45	2.1×10^4	2.8×10^4
50.00	0.360	3.70	4.93	5.17	8.6×10^4	1.5×10^5
70.00	0.568	3.70	5.84	6.25	6.9×10^5	1.8×10^6
80.00	0.692	3.70	6.43	6.96	2.7×10^6	9.0×10^6
90.00	0.835	3.70	7.11	7.76	1.3×10^7	5.8×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.70	3.92	3.96	8.3×10^3	9.2×10^3
20.00	0.089	3.70	4.19	4.28	1.5×10^4	1.9×10^4
30.00	0.144	3.70	4.51	4.67	3.3×10^4	4.7×10^4
50.00	0.281	3.70	5.42	5.75	2.6×10^5	5.6×10^5
70.00	0.477	3.70	6.77	7.35	5.9×10^6	2.3×10^7
80.00	0.610	3.70	7.70	8.46	5.0×10^7	2.9×10^8
90.00	0.779	3.70	8.84	9.82	6.9×10^8	6.6×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.70	3.703	3.704	5.05×10^3	5.05×10^3
0.89	0.0009	3.70	3.709	3.711	5.12×10^3	5.14×10^3
1.77	0.0018	3.70	3.717	3.720	5.21×10^3	5.25×10^3

TABLE XXII

SECOND FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.58	3.76	3.79	5.7×10^3	6.2×10^3
20.00	0.123	3.58	3.98	4.06	9.6×10^3	1.1×10^4
30.00	0.194	3.58	4.24	4.36	1.7×10^4	2.3×10^4
50.00	0.360	3.58	4.87	5.12	7.5×10^4	1.3×10^5
70.00	0.568	3.58	5.82	6.25	6.9×10^5	1.8×10^6
80.00	0.692	3.58	6.44	6.98	2.7×10^6	9.6×10^6
90.00	0.835	3.58	7.16	7.84	1.4×10^7	6.9×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.58	3.80	3.84	6.3×10^3	7.0×10^3
20.00	0.089	3.58	4.07	4.17	1.2×10^4	1.5×10^4
30.00	0.144	3.58	4.41	4.57	2.6×10^4	3.7×10^4
50.00	0.281	3.58	5.34	5.68	2.2×10^5	4.8×10^5
70.00	0.477	3.58	6.73	7.33	5.4×10^6	2.1×10^7
80.00	0.610	3.58	7.75	8.54	5.6×10^7	3.5×10^8
90.00	0.779	3.58	8.90	9.91	7.9×10^8	8.2×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	3.58	3.584	3.584	3.84×10^3	3.85×10^3
0.89	0.0009	3.58	3.591	3.593	3.90×10^3	3.91×10^3
1.77	0.0018	3.58	3.598	3.602	3.97×10^3	4.00×10^3

TABLE XXIII

FIRST FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.08	2.23	2.22	1.7×10^2	1.7×10^2
20.00	0.123	2.08	2.42	2.40	2.6×10^2	2.5×10^2
30.00	0.194	2.08	2.64	2.61	4.3×10^2	4.1×10^2
50.00	0.360	2.08	3.15	3.10	1.4×10^3	1.3×10^3
70.00	0.568	2.08	3.93	3.84	8.5×10^3	7.0×10^3
80.00	0.692	2.08	4.47	4.36	2.9×10^4	2.3×10^4
90.00	0.835	2.08	5.09	4.95	1.2×10^5	8.9×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.08	2.28	2.27	1.9×10^2	1.8×10^2
20.00	0.089	2.08	2.51	2.49	3.3×10^2	3.1×10^2
30.00	0.144	2.08	2.80	2.76	6.3×10^2	5.8×10^2
50.00	0.281	2.08	3.58	3.51	3.8×10^3	3.2×10^3
70.00	0.477	2.08	4.73	4.61	5.4×10^4	4.0×10^4
80.00	0.610	2.08	5.53	5.37	3.4×10^5	2.3×10^5
90.00	0.779	2.08	6.55	6.33	3.5×10^6	2.2×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	2.08	2.082	2.082	1.21×10^2	1.21×10^2
0.89	0.0009	2.08	2.087	2.087	1.22×10^2	1.22×10^2
1.77	0.0018	2.08	2.094	2.094	1.24×10^2	1.24×10^2

TABLE XXIV

FIRST FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.20	2.36	2.35	2.3×10^2	2.2×10^2
20.00	0.123	2.20	2.56	2.54	3.6×10^2	3.5×10^2
30.00	0.194	2.20	2.79	2.76	6.2×10^2	5.8×10^2
50.00	0.360	2.20	3.35	3.30	2.2×10^3	2.0×10^3
70.00	0.568	2.20	4.19	4.10	1.6×10^4	1.2×10^4
80.00	0.692	2.20	4.76	4.64	5.8×10^4	4.4×10^4
90.00	0.835	2.20	5.41	5.25	2.6×10^5	1.8×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.20	2.41	2.40	2.6×10^2	2.5×10^2
20.00	0.089	2.20	2.66	2.64	4.6×10^2	4.3×10^2
30.00	0.144	2.20	2.96	2.93	9.2×10^3	8.4×10^2
50.00	0.281	2.20	3.81	3.73	6.5×10^3	5.4×10^3
70.00	0.477	2.20	5.04	4.92	1.1×10^5	8.2×10^4
80.00	0.610	2.20	5.93	5.75	8.5×10^5	5.6×10^5
90.00	0.779	2.20	7.00	6.77	1.0×10^7	5.9×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	2.20	2.201	2.201	1.59×10^2	1.59×10^2
0.89	0.0009	2.20	2.207	2.207	1.61×10^2	1.61×10^2
1.77	0.0018	2.20	2.214	2.214	1.64×10^2	1.64×10^2

TABLE XXV

FIRST FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.32	2.49	2.48	3.1×10^2	3.0×10^2
20.00	0.123	2.32	2.70	2.69	5.1×10^2	4.8×10^2
30.00	0.194	2.32	2.95	2.92	8.9×10^2	8.3×10^2
50.00	0.360	2.32	3.55	3.49	3.6×10^3	3.1×10^3
70.00	0.568	2.32	4.46	4.36	2.9×10^4	2.3×10^4
80.00	0.692	2.32	5.05	4.92	1.1×10^5	8.4×10^4
90.00	0.835	2.32	5.73	5.57	5.4×10^5	3.7×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	2,32	2.54	2.53	3.5×10^2	3.4×10^2
20.00	0.089	2.32	2.81	2.79	6.4×10^2	6.2×10^2
30.00	0.144	2.32	3.13	3.10	1.4×10^3	1.2×10^3
50.00	0.281	2.32	4.04	3.96	1.1×10^4	9.1×10^3
70.00	0.477	2.32	5.39	5.24	2.5×10^5	1.8×10^5
80.00	0.610	2.32	6.32	6.13	2.1×10^6	1.4×10^6
90.00	0.779	2.32	7.46	7.21	2.9×10^7	1.6×10^7

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	2.32	2.323	2.323	2.10×10^2	2.10×10^2
0.89	0.0009	2.32	2.329	2.329	2.13×10^2	2.13×10^2
1.77	0.0018	2.32	2.337	2.336	2.17×10^2	2.17×10^2

TABLE XXVI

FIRST FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.51	2.69	2.68	4.9×10^2	4.8×10^2
20.00	0.123	2.51	2.91	2.89	8.2×10^2	7.8×10^2
30.00	0.194	2.51	3.17	3.13	1.5×10^3	1.4×10^3
50.00	0.360	2.51	3.80	3.74	6.4×10^3	5.5×10^3
70.00	0.568	2.51	4.75	4.65	5.7×10^4	4.4×10^4
80.00	0.692	2.51	5.37	5.23	2.3×10^5	1.7×10^5
90.00	0.835	2.51	6.09	5.92	1.2×10^6	8.3×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.51	2.73	2.72	5.4×10^2	5.3×10^2
20.00	0.089	2.51	3.00	2.98	1.0×10^3	9.5×10^2
30.00	0.144	2.51	3.34	3.30	2.2×10^3	2.0×10^3
50.00	0.281	2.51	4.27	4.19	1.9×10^4	1.5×10^4
70.00	0.477	2.51	5.66	5.51	4.6×10^5	3.2×10^5
80.00	0.610	2.51	6.68	6.48	4.8×10^6	3.0×10^6
90.00	0.779	2.51	7.83	7.58	6.7×10^7	3.8×10^7

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_1	Log K_1^*		K_1^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	2.51	2.514	2.514	3.27×10^2	3.27×10^2
0.89	0.0009	2.51	2.521	2.520	3.32×10^2	3.31×10^2
1.77	0.0018	2.51	2.528	2.528	3.38×10^2	3.37×10^2

TABLE XXVI

SECOND FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.43	1.58	1.57	3.8×10^1	3.8×10^1
20.00	0.123	1.43	1.77	1.75	5.9×10^1	5.7×10^1
30.00	0.194	1.43	1.98	1.96	9.7×10^1	9.1×10^1
50.00	0.360	1.43	2.50	2.45	3.2×10^2	2.8×10^2
70.00	0.568	1.43	3.28	3.19	1.9×10^3	1.6×10^3
80.00	0.692	1.43	3.82	3.71	6.6×10^3	5.1×10^3
90.00	0.835	1.43	4.44	4.30	2.8×10^4	2.0×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.43	1.63	1.62	4.2×10^1	4.1×10^1
20.00	0.089	1.43	1.86	1.84	7.3×10^1	6.9×10^1
30.00	0.144	1.43	2.15	2.11	1.4×10^2	1.3×10^2
50.00	0.281	1.43	2.93	2.86	8.5×10^2	7.2×10^2
70.00	0.477	1.43	4.08	3.96	1.2×10^4	9.1×10^3
80.00	0.610	1.43	4.88	4.72	7.7×10^4	5.3×10^4
90.00	0.779	1.43	5.90	5.68	7.9×10^5	4.8×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.43	1.432	1.432	2.70×10^1	2.70×10^1
0.89	0.0009	1.43	1.437	1.437	2.74×10^1	2.73×10^1
1.77	0.0018	1.43	1.444	1.444	2.78×10^1	2.78×10^1

TABLE XXVIII

SECOND FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.55	1.71	1.70	5.1×10^1	5.0×10^1
20.00	0.123	1.55	1.91	1.89	8.1×10^1	7.8×10^1
30.00	0.194	1.55	2.14	2.11	1.4×10^2	1.3×10^2
50.00	0.360	1.55	2.70	2.65	5.0×10^2	4.4×10^2
70.00	0.568	1.55	3.54	3.45	3.5×10^3	2.8×10^3
80.00	0.692	1.55	4.11	3.99	1.3×10^4	9.8×10^3
90.00	0.835	1.55	4.76	4.60	5.7×10^4	4.0×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.55	1.76	1.75	5.7×10^1	5.6×10^1
20.00	0.089	1.55	2.01	1.99	1.0×10^2	9.7×10^1
30.00	0.144	1.55	2.31	2.28	2.0×10^2	1.9×10^2
50.00	0.281	1.55	3.16	3.08	1.4×10^3	1.2×10^3
70.00	0.477	1.55	4.40	4.27	2.5×10^4	1.8×10^4
80.00	0.610	1.55	5.28	5.10	1.9×10^5	1.3×10^5
90.00	0.779	1.55	6.35	6.12	2.2×10^6	1.3×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.55	1.551	1.551	3.56×10^1	3.56×10^1
0.89	0.0009	1.55	1.557	1.557	3.61×10^1	3.60×10^1
1.77	0.0018	1.55	1.564	1.564	3.67×10^1	3.66×10^1

TABLE XXIX

SECOND FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.67	1.84	1.83	6.9×10^1	6.8×10^1
20.00	0.123	1.67	2.05	2.04	1.1×10^2	1.1×10^2
30.00	0.194	1.67	2.30	2.27	2.0×10^2	1.9×10^2
50.00	0.360	1.67	2.90	2.84	8.0×10^2	7.0×10^2
70.00	0.568	1.67	3.81	3.71	6.5×10^3	5.1×10^3
80.00	0.692	1.67	4.40	4.27	2.5×10^4	1.9×10^4
90.00	0.835	1.67	5.08	4.92	1.2×10^5	8.3×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.67	1.89	1.88	7.8×10^1	7.6×10^1
20.00	0.089	1.67	2.16	2.14	1.4×10^2	1.4×10^2
30.00	0.144	1.67	2.48	2.45	3.0×10^2	2.8×10^2
50.00	0.281	1.67	3.39	3.31	2.5×10^3	2.0×10^3
70.00	0.610	1.67	4.74	4.59	5.5×10^4	3.9×10^4
80.00	0.610	1.67	5.67	5.48	4.7×10^5	3.0×10^5
90.00	0.779	1.67	6.81	6.56	6.4×10^6	3.7×10^7

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.67	1.673	1.673	4.71×10^1	4.71×10^1
0.89	0.0009	1.67	1.679	1.679	4.78×10^1	4.77×10^1
1.77	0.0018	1.67	1.687	1.686	4.86×10^1	4.85×10^1

TABLE XXX

SECOND FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.86	2.04	2.03	1.1×10^2	1.1×10^2
20.00	0.123	1.86	2.26	2.24	1.8×10^2	1.8×10^2
30.00	0.194	1.86	2.52	2.48	3.3×10^2	3.0×10^3
50.00	0.360	1.86	3.15	3.09	1.4×10^3	1.2×10^3
70.00	0.568	1.86	4.10	4.00	1.3×10^4	1.0×10^4
80.00	0.692	1.86	4.72	4.58	5.2×10^4	3.8×10^4
90.00	0.835	1.86	5.44	5.27	2.7×10^5	1.8×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.86	2.08	2.07	1.2×10^2	1.2×10^2
20.00	0.089	1.86	2.35	2.33	2.3×10^2	2.1×10^2
30.00	0.144	1.86	2.69	2.65	4.9×10^2	4.5×10^2
50.00	0.281	1.86	3.62	3.54	4.2×10^3	3.5×10^3
70.00	0.477	1.86	5.01	4.86	1.0×10^5	7.2×10^5
80.00	0.610	1.86	6.03	5.83	1.1×10^6	6.8×10^6
90.00	0.779	1.86	7.18	6.92	1.5×10^7	8.4×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K_2	Log K_2^*		K_2^*	
			Exptl	Calcd	Exptl	Calcd
0.18	0.0002	1.86	1.864	1.864	7.32×10^1	7.31×10^1
0.89	0.0009	1.86	1.871	1.870	7.42×10^1	7.41×10^1
1.77	0.0018	1.86	1.878	1.877	7.56×10^1	7.54×10^1

TABLE XXXI

AVERAGE FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.38	1.37	2.4×10^1	2.3×10^1
20.00	0.123	1.57	1.54	3.7×10^1	3.5×10^1
30.00	0.194	1.79	1.73	6.2×10^1	5.4×10^1
50.00	0.360	2.30	2.20	2.0×10^2	1.6×10^2
70.00	0.568	3.08	2.91	1.2×10^3	8.1×10^2
80.00	0.692	3.62	3.39	4.2×10^3	2.4×10^3
90.00	0.835	4.24	3.95	1.7×10^4	8.9×10^3

ETHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.43	1.41	2.7×10^1	2.6×10^1
20.00	0.089	1.66	1.62	4.6×10^1	4.2×10^1
30.00	0.144	1.95	1.88	8.9×10^1	7.6×10^1
50.00	0.281	2.73	2.59	5.4×10^2	3.9×10^2
70.00	0.477	3.88	3.63	7.6×10^3	4.3×10^3
80.00	0.610	4.68	4.36	4.8×10^4	2.3×10^4
90.00	0.779	5.70	5.27	5.0×10^5	1.9×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.232	1.232	1.71×10^1	1.71×10^1
0.0089	0.0009	1.237	1.236	1.73×10^1	1.72×10^1
0.0177	0.0018	1.244	1.243	1.75×10^1	1.75×10^1

TABLE XXXII

AVERAGE FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.51	1.49	3.2×10^1	3.1×10^1
20.00	0.123	1.71	1.66	5.1×10^1	4.6×10^1
30.00	0.194	1.94	1.88	8.7×10^1	7.6×10^1
50.00	0.360	2.50	2.39	3.2×10^2	2.4×10^2
70.00	0.568	3.34	3.15	2.2×10^3	1.4×10^3
80.00	0.692	3.91	3.67	8.1×10^3	4.7×10^3
90.00	0.835	4.56	4.25	3.6×10^4	1.7×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.56	1.54	3.6×10^1	3.5×10^1
20.00	0.089	1.81	1.77	6.5×10^1	5.9×10^1
30.00	0.144	2.11	2.04	1.3×10^2	1.1×10^2
50.00	0.281	2.96	2.81	9.1×10^2	6.5×10^2
70.00	0.477	4.20	3.93	1.6×10^4	8.5×10^3
80.00	0.610	5.08	4.72	1.2×10^5	5.2×10^4
90.00	0.779	6.15	5.69	1.4×10^6	4.9×10^5

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.351	1.351	2.24×10^1	2.24×10^1
0.0089	0.0009	1.357	1.356	2.28×10^1	2.27×10^1
0.0177	0.0018	1.364	1.363	2.31×10^1	2.31×10^1

TABLE XXXIII

AVERAGE FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.68	1.66	4.8×10^1	4.6×10^1
20.00	0.123	1.89	1.86	7.8×10^1	7.2×10^1
30.00	0.194	2.14	2.08	1.4×10^2	1.2×10^2
50.00	0.360	2.74	2.63	5.5×10^2	4.3×10^2
70.00	0.568	3.65	3.45	4.5×10^3	2.8×10^3
80.00	0.692	4.24	3.98	1.7×10^4	9.6×10^3
90.00	0.835	4.92	4.60	8.3×10^4	4.0×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.73	1.71	5.4×10^1	5.1×10^1
20.00	0.089	2.00	1.95	1.0×10^2	8.9×10^1
30.00	0.144	2.32	2.25	2.1×10^2	1.8×10^2
50.00	0.281	3.23	3.07	1.7×10^3	1.2×10^3
70.00	0.477	4.58	4.29	3.8×10^4	2.0×10^4
80.00	0.610	5.51	5.13	3.2×10^5	1.4×10^5
90.00	0.779	6.65	6.16	4.5×10^6	1.5×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.513	1.513	3.26×10^1	3.26×10^1
0.0089	0.0009	1.519	1.518	3.30×10^1	3.30×10^1
0.0177	0.0018	1.527	1.525	3.37×10^1	3.35×10^1

TABLE XXXIV

AVERAGE FORMATION CONSTANTS OF CALCIUM COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.87	1.85	7.5×10^1	7.2×10^1
20.00	0.123	2.09	2.05	1.2×10^2	1.1×10^2
30.00	0.194	2.35	2.28	2.3×10^2	1.9×10^2
50.00	0.360	2.98	2.86	9.7×10^2	7.3×10^2
70.00	0.568	3.93	3.72	8.6×10^3	5.3×10^3
80.00	0.692	4.55	4.27	3.6×10^4	1.9×10^4
90.00	0.835	5.27	4.93	1.9×10^5	8.6×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.91	1.89	8.2×10^1	7.8×10^1
20.00	0.089	2.18	2.14	1.5×10^2	1.4×10^2
30.00	0.144	2.52	2.44	3.4×10^2	2.8×10^2
50.00	0.281	3.45	3.29	2.8×10^3	2.0×10^3
70.00	0.477	4.84	4.54	7.0×10^4	3.5×10^4
80.00	0.610	5.86	5.46	7.3×10^5	2.9×10^5
90.00	0.779	7.01	6.50	1.0×10^7	3.2×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.699	1.699	5.00×10^1	5.00×10^1
0.0089	0.0009	1.706	1.705	5.08×10^1	5.07×10^1
0.0177	0.0018	1.713	1.712	5.17×10^1	5.15×10^1

TABLE XXXV

AVERAGE FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	4.07	4.10	1.2×10^4	1.3×10^4
20.00	0.123	4.26	4.32	1.8×10^4	2.1×10^4
30.00	0.194	4.47	4.58	3.0×10^4	3.8×10^4
50.00	0.360	4.99	5.20	9.8×10^4	1.6×10^5
70.00	0.568	5.77	6.12	5.9×10^5	1.3×10^6
80.00	0.692	6.31	6.76	2.0×10^6	5.8×10^6
90.00	0.835	6.93	7.50	8.5×10^6	3.2×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	4.12	4.15	1.3×10^4	1.4×10^4
20.00	0.089	4.35	4.43	2.2×10^4	2.7×10^4
30.00	0.144	4.64	4.77	4.4×10^4	5.9×10^4
50.00	0.281	5.42	5.71	2.6×10^5	5.1×10^5
70.00	0.477	6.57	7.08	3.7×10^6	1.2×10^7
80.00	0.610	7.37	8.03	2.3×10^7	1.1×10^8
90.00	0.779	8.39	9.24	2.4×10^8	1.7×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	3.922	3.922	8.36×10^3	8.36×10^3
0.0089	0.0009	3.927	3.927	8.45×10^3	8.49×10^3
0.0177	0.0018	3.934	3.937	8.59×10^3	8.65×10^3

TABLE XXXVI

AVERAGE FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.89	3.92	7.8×10^3	8.3×10^3
20.00	0.123	4.09	4.16	1.2×10^4	1.4×10^4
30.00	0.194	4.32	4.43	2.1×10^4	2.7×10^4
50.00	0.360	4.88	5.10	7.6×10^4	1.3×10^5
70.00	0.568	5.72	6.10	5.2×10^5	1.3×10^6
80.00	0.692	6.29	6.78	2.0×10^6	6.0×10^6
90.00	0.835	6.94	7.55	8.7×10^6	3.6×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.94	3.98	8.7×10^3	9.6×10^3
20.00	0.089	4.19	4.28	1.6×10^4	1.9×10^4
30.00	0.144	4.49	4.64	3.1×10^4	4.4×10^4
50.00	0.281	5.34	5.65	2.2×10^5	4.5×10^5
70.00	0.477	6.58	7.12	3.8×10^6	1.3×10^7
80.00	0.610	7.46	8.17	2.9×10^7	1.5×10^8
90.00	0.779	8.53	9.44	3.4×10^8	2.8×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	3.731	3.732	5.38×10^3	5.40×10^3
0.0089	0.0009	3.737	3.739	5.46×10^3	5.48×10^3
0.0177	0.0018	3.744	3.747	5.55×10^3	5.58×10^3

TABLE XXXVII

AVERAGE FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.78	3.81	6.0×10^3	6.5×10^3
20.00	0.123	3.99	4.07	9.8×10^3	1.2×10^3
30.00	0.194	4.24	5.08	1.7×10^4	2.3×10^4
50.00	0.360	4.84	5.08	6.9×10^4	1.2×10^5
70.00	0.568	5.75	6.16	5.6×10^5	1.4×10^6
80.00	0.692	6.34	6.87	2.2×10^6	7.4×10^6
90.00	0.835	7.02	7.67	1.0×10^7	4.7×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.83	3.87	6.8×10^3	7.4×10^3
20.00	0.089	4.10	4.19	1.3×10^4	1.6×10^4
30.00	0.144	4.42	4.58	2.6×10^4	3.8×10^4
50.00	0.281	5.33	5.66	2.1×10^5	4.6×10^5
70.00	0.477	6.68	7.26	4.8×10^6	1.8×10^7
80.00	0.610	7.51	8.37	4.1×10^7	2.3×10^8
90.00	0.779	8.75	9.73	5.6×10^8	5.4×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	3.613	3.614	4.10×10^3	4.11×10^3
0.0089	0.0009	3.619	3.621	4.16×10^3	4.18×10^3
0.0177	0.0018	3.627	3.630	4.24×10^3	4.27×10^3

TABLE XXXVII

AVERAGE FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	3.67	3.70	4.7×10^3	5.0×10^3
20.00	0.123	3.89	3.97	7.8×10^3	9.3×10^3
30.00	0.194	4.15	4.27	1.4×10^4	1.9×10^4
50.00	0.360	4.78	5.03	6.0×10^4	1.1×10^5
70.00	0.568	5.73	6.16	5.4×10^5	1.4×10^6
80.00	0.692	6.35	6.89	2.2×10^6	7.8×10^6
90.00	0.835	7.07	7.75	1.2×10^7	5.6×10^7

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	3.71	3.75	5.1×10^3	5.6×10^3
20.00	0.089	3.98	4.08	9.6×10^3	1.2×10^4
30.00	0.144	4.32	4.48	2.1×10^4	3.0×10^4
50.00	0.281	5.25	5.59	1.8×10^5	3.9×10^5
70.00	0.477	6.664	7.24	4.4×10^6	1.7×10^7
80.00	0.610	7.66	8.45	4.6×10^7	2.8×10^8
90.00	0.779	8.81	9.82	6.5×10^8	6.6×10^9

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	3.494	3.495	3.12×10^3	3.13×10^3
0.0089	0.0009	3.501	3.503	3.17×10^3	3.18×10^3
0.0177	0.0018	3.508	3.512	3.22×10^3	3.25×10^3

TABLE XXXIX

AVERAGE FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 15°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	1.90	1.89	8.0×10^1	7.8×10^1
20.00	0.123	2.09	2.07	1.2×10^2	1.2×10^2
30.00	0.194	2.31	2.28	2.0×10^2	1.9×10^2
50.00	0.360	2.82	2.77	6.7×10^2	6.0×10^2
70.00	0.568	3.60	3.51	4.0×10^3	3.3×10^3
80.00	0.692	4.14	4.03	1.4×10^4	1.1×10^4
90.00	0.835	4.76	4.62	5.8×10^4	4.2×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	1.95	1.94	9.0×10^1	8.8×10^1
20.00	0.089	2.18	2.16	1.5×10^2	1.5×10^2
30.00	0.144	2.47	2.43	3.0×10^2	2.7×10^2
50.00	0.281	3.25	3.18	1.8×10^3	1.5×10^3
70.00	0.477	4.40	4.28	2.5×10^4	1.9×10^4
80.00	0.610	5.20	5.04	1.6×10^5	1.1×10^5
90.00	0.779	6.22	6.00	1.7×10^6	1.0×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.757	1.757	5.71×10^1	5.71×10^1
0.0089	0.0009	1.762	1.762	5.78×10^1	5.78×10^1
0.0177	0.0018	1.769	1.769	5.78×10^1	5.87×10^1

TABLE XL

AVERAGE FORMATION CONSTANTS OF IRON COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 25°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.03	2.02	1.1×10^2	1.1×10^2
20.00	0.123	2.23	2.21	1.7×10^2	1.6×10^2
30.00	0.194	2.46	2.43	2.9×10^2	2.7×10^2
50.00	0.360	3.02	2.97	1.1×10^3	9.4×10^2
70.00	0.568	3.86	3.77	7.3×10^3	6.0×10^3
80.00	0.692	4.43	4.31	2.7×10^4	2.1×10^4
90.00	0.835	5.08	4.92	1.2×10^5	8.4×10^4

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.08	2.07	1.2×10^2	1.2×10^2
20.00	0.089	2.33	2.31	2.2×10^2	2.1×10^2
30.00	0.144	2.63	2.60	4.3×10^2	4.0×10^2
50.00	0.281	3.48	3.40	3.0×10^3	2.5×10^3
70.00	0.477	4.72	4.59	5.3×10^4	3.9×10^4
80.00	0.610	5.60	5.42	4.0×10^5	2.7×10^5
90.00	0.779	6.67	6.44	4.7×10^6	2.8×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.876	1.876	7.52×10^1	7.52×10^1
0.0089	0.0009	1.882	1.882	7.62×10^1	7.62×10^1
0.0177	0.0018	1.889	1.889	7.74×10^1	7.74×10^1

TABLE XLI

AVERAGE FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 35°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.056	2.16	2.15	1.5×10^2	1.4×10^2
20.00	0.123	2.37	2.36	2.4×10^2	2.3×10^2
30.00	0.194	2.62	2.59	4.2×10^2	3.9×10^2
50.00	0.360	3.22	3.16	1.7×10^3	1.5×10^3
70.00	0.568	4.13	4.03	1.4×10^4	3.9×10^4
80.00	0.692	4.72	4.59	5.3×10^4	3.9×10^4
90.00	0.835	5.40	5.24	2.5×10^5	1.8×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.21	2.20	1.6×10^2	1.6×10^2
20.00	0.089	2.48	2.46	3.0×10^2	2.9×10^2
30.00	0.144	2.80	2.77	6.4×10^2	6.0×10^2
50.00	0.281	3.71	3.63	5.2×10^3	4.3×10^3
70.00	0.477	5.06	4.91	1.2×10^5	8.2×10^4
80.00	0.610	5.99	5.80	9.9×10^5	6.4×10^5
90.00	0.779	7.13	6.88	1.4×10^7	7.7×10^6

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	1.998	1.998	9.95×10^1	9.95×10^1
0.0089	0.0009	2.004	2.004	1.01×10^2	1.01×10^2
0.0177	0.0018	2.012	2.011	1.03×10^2	1.03×10^2

TABLE XLII

AVERAGE FORMATION CONSTANTS OF ZINC COMPLEXES OF LACTIC ACID IN VARIOUS MIXED SOLVENT MEDIA AT A TEMPERATURE OF 40°C

METHANOL-WATER

WT% MeOH	MF MeOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.059	2.36	2.35	2.3×10^2	2.3×10^2
20.00	0.123	2.58	2.56	3.8×10^2	3.7×10^2
30.00	0.194	2.84	2.80	7.0×10^2	6.4×10^2
50.00	0.360	3.47	3.41	3.0×10^3	2.6×10^3
70.00	0.568	4.42	4.32	2.7×10^4	2.1×10^4
80.00	0.692	5.04	4.90	1.1×10^5	8.0×10^4
90.00	0.835	5.76	5.59	5.8×10^5	3.9×10^5

ETHANOL-WATER

WT% EtOH	MF EtOH	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
10.00	0.042	2.40	2.39	2.5×10^2	2.5×10^2
20.00	0.089	2.67	2.65	4.7×10^2	4.5×10^2
30.00	0.144	3.01	2.97	1.0×10^3	9.4×10^2
50.00	0.281	3.94	3.86	8.8×10^3	7.3×10^3
70.00	0.477	5.33	5.18	2.2×10^5	1.5×10^5
80.00	0.610	6.35	6.15	2.3×10^7	1.4×10^6
90.00	0.779	7.50	7.25	3.2×10^7	1.8×10^7

GLUCOSE-WATER

WT% Glucose	MF Glucose	Log K^*_{av}		K^*_{av}	
		Exptl	Calcd	Exptl	Calcd
0.0018	0.0002	2.189	2.189	1.55×10^2	1.55×10^2
0.0089	0.0009	2.196	2.195	1.57×10^2	1.57×10^2
0.0177	0.0018	2.203	2.203	1.60×10^2	1.60×10^2

CHAPTER V

DISCUSSION AND CONCLUSIONS

Two distinct equilibrium constants for the formation of each of the metal lactates were observed in this study. First, we will review the published work on the metal complexes of lactic acid; this will then be followed by a discussion of the results obtained in our investigation.

Iron (III) Lactate

Iron (III) lactate appears to be the most disputed of the three metal lactates which we studied, and was found by us to exhibit the most erratic behavior and to deviate to the greatest extent from the correlating relationship which we are testing. Andrei and Barnes (32) reported the formation of a 1:1 complex $FeML^{2+}$ (where M_2L = lactic acid) by the elimination of one H^+ ion from lactic acid. They proposed the structure depicted in Figure 8 for this complex. Bertin-Batsch (35) also observed a 1:1 complex of iron (III) and lactic acid, and determined that its instability constant (the inverse of the formation constant) was $K_{inst} = 10^{-6.9}$. Pimenta (82) has stated that only the 1:1 complex of iron lactate exists at very low pH (near the range from 2.00 to 2.05). Pyatnitskii and Kolomiets (84) have observed and reported a two-stage dissociation of the ferric lactate complex, whose structure, according to these authors, is given in Figure 9. Their data is given in Table XLIII.

TABLE XLIII: Instability Constants of Ferric Lactate Complexes (84)

K_{inst}	Formula	pH Range
$K_1 = 2.7 \pm 0.8 \times 10^{-4}$	$FeHL^{2+}$	4.00-5.00

FIGURE 8:

STRUCTURE OF $FeML^{2+}$ COORDINATION COMPLEX

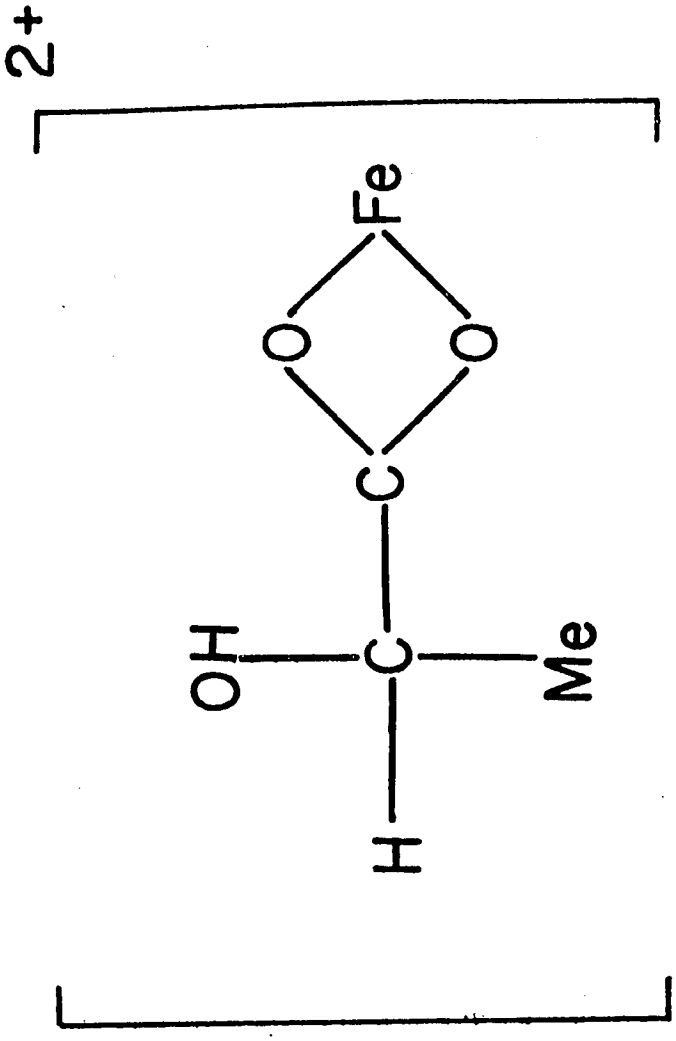
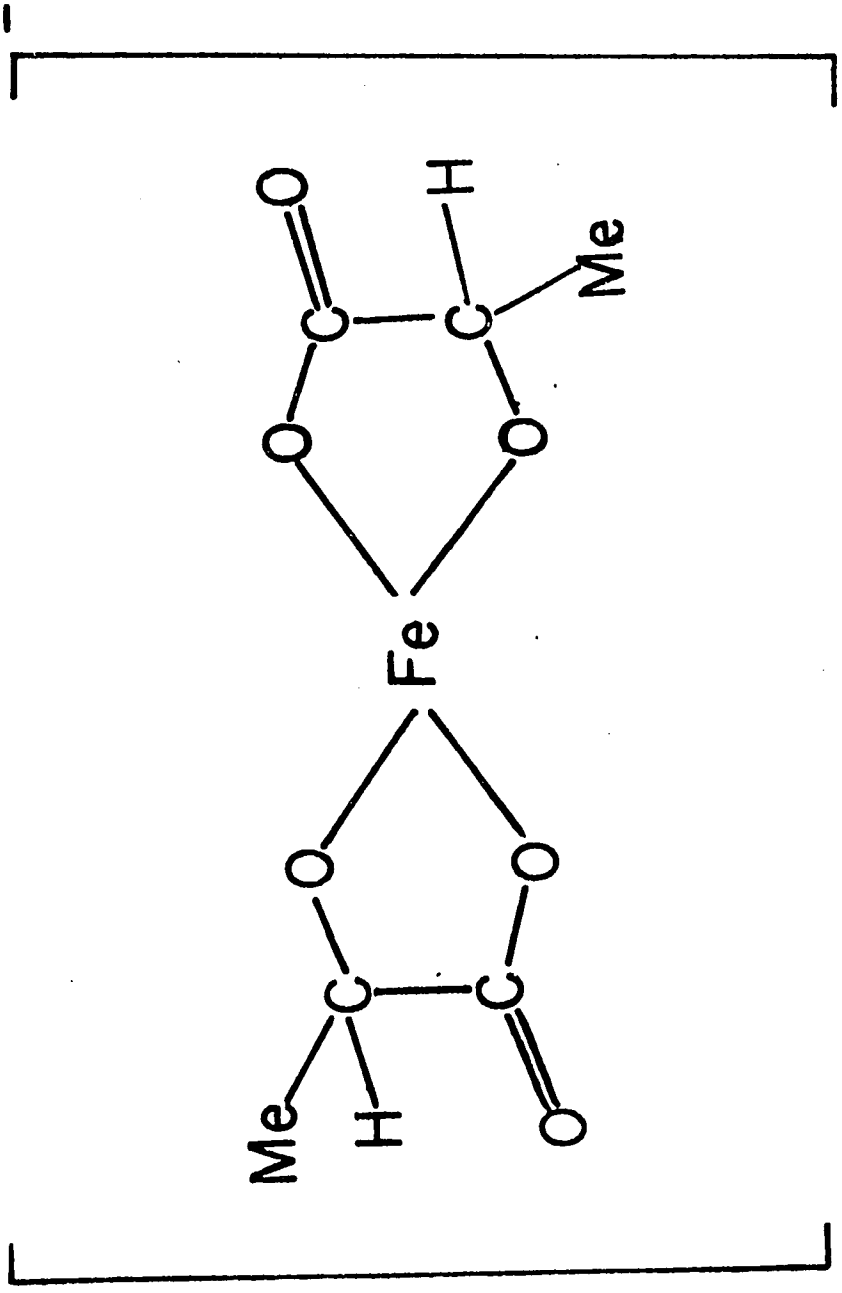

2+
Fe
O
O
C
OH
C
Me
H

FIGURE 9:

STRUCTURE OF FeL_2^- COORDINATION COMPLEX


O
H
Me
C
C
O
O
Fe
O
O
C
C
Me
H
O

$K_2 = 7.1 \pm 0.4 \times 10^{-27}$ FeL_2^- 4.00-5.00

It would seem from the data that the bidentate chelate complex of iron would be extremely stable (as indicated by its small instability constant). It has been claimed by Trifanov and Vitanov (105) that three distinct complexes of iron and lactic acid exist--I, $FeHL^{2+}$; II, $Fe(HL)_2^+$; and III, $Fe(HL)_3$. However, in the aforementioned study, only the first instability constant for the initial stage of dissociation had been determined (and was reported as K_{inst} for $I = 2.02 \times 10^{-5}$). Hence, it may be concluded that only the presence of the monodentate complex (I) of iron (III) lactate has been definitely established, and the role of the -OH group, if any, has not been established.

Calcium (II) Lactate

Formation of calcium lactate has been studied more extensively, probably due to its biological significance in that it is the dispersive agent responsible for the distribution of calcium within the body. Ghosh and Nair (5) have written excellent treatise on the formation constants of calcium lactate, as determined from data collected by taking conductivity measurements. The scope of their investigation was limited to aqueous media, but their study did serve as a source for the formation constant data of calcium lactate in water.

Zinc (II) Lactate

As with calcium, the number of steps in the formation of zinc (II) lactate appears to be less disputed. Wark (110) claims to have prepared bidentate complexes of zinc with lactic acid behaving as a bidentate ligand, but offered no structural details, nor data regarding the formation constants for zinc-lactic acid complexes. At a pH of 7.4 and an

ionic strength of 0.16, they reported that log K_1 = 1.60 and log K_2 = 1.90 in aqueous media. These results did not, however, correspond to the system which we required as our reference standard (namely, zinc lactate in pure water at infinite dilution and zero ionic strength), nor did they study the temperature dependence of log K_1 and log K_2. Bonniol and Vielen (39) found that, at 25°C and zero ionic strength, log K_1 equals 2.20 and log K_2 equals 1.55. The discrepancy between the results reported by these investigators may be attributed, in part at least, to the neutral salt effect (or diverse ion effect)(1), which would increase the dissociation of the complex, thereby increasing the value of the instability constant (i.e., decreasing the value of the formation constant.

The primary goal of this study was to obtain a function that would correlate K^*_{av} (the value of the average formation constant in a mixed solvent system at infinite dilution and zero ionic strength) to K_{av} (the value of the average formation constant in aqueous solution at infinite dilution and zero ionic strength). To achieve this goal, plots were made of log K^*_{av} against various functions of the bulk dielectric constant of the medium. Certain criteria were established to which the functions should conform; the criteria for an acceptable plot are:

(1) it should be continuous;

(2) it should have no maximum or minimum;

(3) it should contain values from as many mixed solvent systems as possible;

(4) it should preferably be linear;

(5) it should be capable of being interpreted in terms of a given model depicting the physical process of complex formation

(e.g., the Born model as described earlier).

After investigating a number of trial functions, Sen and Adcock (93) have demonstrated that only a Born-type equation correlates the ionization constants of the organic monoprotic acids as functions of the bulk dielectric constants of the solvent media. Some of the plots were tested by them and found to be unsatisfactory were:

K_i/K_i^* versus ϵ^*; pK_i^* versus ϵ^*; pK_i^* versus ϵ^{*2};
K_i/K_i^* versus log ϵ^*; pK_i^* versus log ϵ^*; pK_i versus ϵ^*; and
K_i/K_i^* versus $1/\epsilon^*$.

The plot which showed the greatest promise of fulfilling most of the criteria proposed for an acceptable curve was that of pK_i^* against $(1/\epsilon^* - 1/\ )$. A corresponding plot in the case of formation constants of the metal complexes should be log K_{av}^* versus $(1/\epsilon^* - 1/\epsilon)$, which would be quite analogous to graphing the Born equation (92).

Figure 6 illustrates the plot of pC_A versus $\bar{n}$ (commonly known as degree of formation curve) for zinc lactate complex in 30 percent ethanol-water at 25°C and an ionic strength of 0.050. The values of log K_1 and log K_2 are directly read from the degree of formation curves; their respective numerical values correspond to pC_A at $n = 0.5$ (for log K_1) and $\bar{n} = 1.5$ (for log K_2) (cf. Chapter II).

The square root of the product of K_1 and K_2 is defined as K_{av} in such a way that it is symmetrically intermediate between K_1 and K_2. It is related to the successive formation constants and the overall formation constant by the relation

$$K_{ov} = K_1 \cdot K_2 = K_{av}^2 \qquad (88)$$

The value for log K_{av} was plotted against the square root of the ionic strength of the solution in which its value was determined, and the plot

was then extrapolated to zero ionic strength in order to yield the value of log K_{av} at infinite dilution. Figure 7 is a graph of one such plot. The values of the formation constants decreased with increasing ionic strength for all the complexes, as was predicted by the Debye-Huckel theory (12):

If the formation of ML is given by

$$M + L \rightleftharpoons ML$$

the formation constant is given by

$$K_f = \frac{a_{ML}}{a_M \cdot a_L} = \frac{C_{ML}}{C_M \cdot C_L} \cdot \frac{\gamma_{ML}}{\gamma_M \cdot \gamma_L} \tag{89}$$

in terms of the activity coefficients of the reacting species. If we now substitute the mean activity coefficient for each of the individual activity coefficients, we have

$$K_f = \frac{C_{ML}}{C_M \cdot C_L} \quad \frac{1}{\gamma_{\pm}^2} \tag{90}$$

assuming that the activity coefficient of the resulting neutral complex is equal to one. From the Debye-Huckel equation(20),

$$\gamma_{\pm} = - 0.509 \left|z_+ z_-\right| \mu^{1/2} \tag{91}$$

or, squaring both sides of equation (91)

$$\gamma_{\pm}^2 = - 0.259 \left|z_+ z_-\right|^2 \mu \tag{92}$$

where u is the ionic strength of the system. Substituting these results into equation (90) yields

$$K_f = \frac{C_{ML}}{C_M \cdot C_L} \quad \frac{1}{0.258 \left|z_+ z_-\right|^2 \mu} \tag{93}$$

It is obvious from equation (93) that as the ionic strength u increases, the magnitude of the formation constant K_f will decrease.

Plots of log K_{av}^* of zinc lactate at 25°C versus the difference of the reciprocals of the bulk dielectric constants ($1/\epsilon^* - 1/\epsilon$) of the

mixed solvent (ϵ^*) and water (ϵ), are shown in Figures 10, 11, and 12. ϵ^* is the value of the bulk dielectric constant of the mixed solvent in which the corresponding K^*_{av} was determined. The plots shown in Figures 10, 11, and 12 correspond to three mixed solvent systems (methanol-water, ethanol-water, and glucose-water), covering the composition ranges of 10 to 90 percent of methanol, 10 to 90 percent of ethanol, and 0.18 to 1.77 percent of glucose. The dielectric constants ranged from 77.68 to 32.56 for methanol-water systems, 76.41 to 25.64 for ethanol-water systems, and 81.77 to 73.24 for glucose-water systems. The plots of log K^*_{av} versus $(1/\epsilon^* - 1/\epsilon)$ for all three metal complexes in all three mixed solvent systems at 15°C, 25°C, 35°C, and 40°C were found to be linear in the dielectric constant ranges mentioned above.

The appropriate equation for these linear plots (Figures 10, 11, and 12) should have the form

$$\log K^*_{av} = \log K + \beta'(1/\epsilon^* - 1/\epsilon) \qquad (94)$$

It is quite obvious that when $\epsilon^* = \epsilon$ log K^*_{av} = log K, which is the y-axis intercept in equation (94). It is also obvious that log K is the average formation constant log K_{av} of the complex in pure water, since only in that case does ϵ^* equal ϵ. The extrapolated values of log K_{av} turn out to be 1.60 ($K_{av} = 0.40 \times 10^2$), 1.72 ($K_{av} = 0.52 \times 10^2$) and 1.55 ($K_{av} = 0.36 \times 10^2$) from the three representative plots. This order of closeness of agreement among the extrapolated values of K_{av} is considered by us as excellent. The value of β' is 210 for the case of Zn (II) complexes, 190 for the case of the Ca (II) complexes, and 250 for the case of the Fe (III) complexes, which corresponds to the slope of the given log K_{av} versus $(1/\epsilon^* - 1/\epsilon)$ plot.

FIGURE 10:

PLOT OF LOG K_{av}^{*} VERSUS $(1/\epsilon^{*} - 1/\epsilon)$ FOR ZINC

(II) LACTATES IN METHANOL-WATER MIXED SOLVENTS

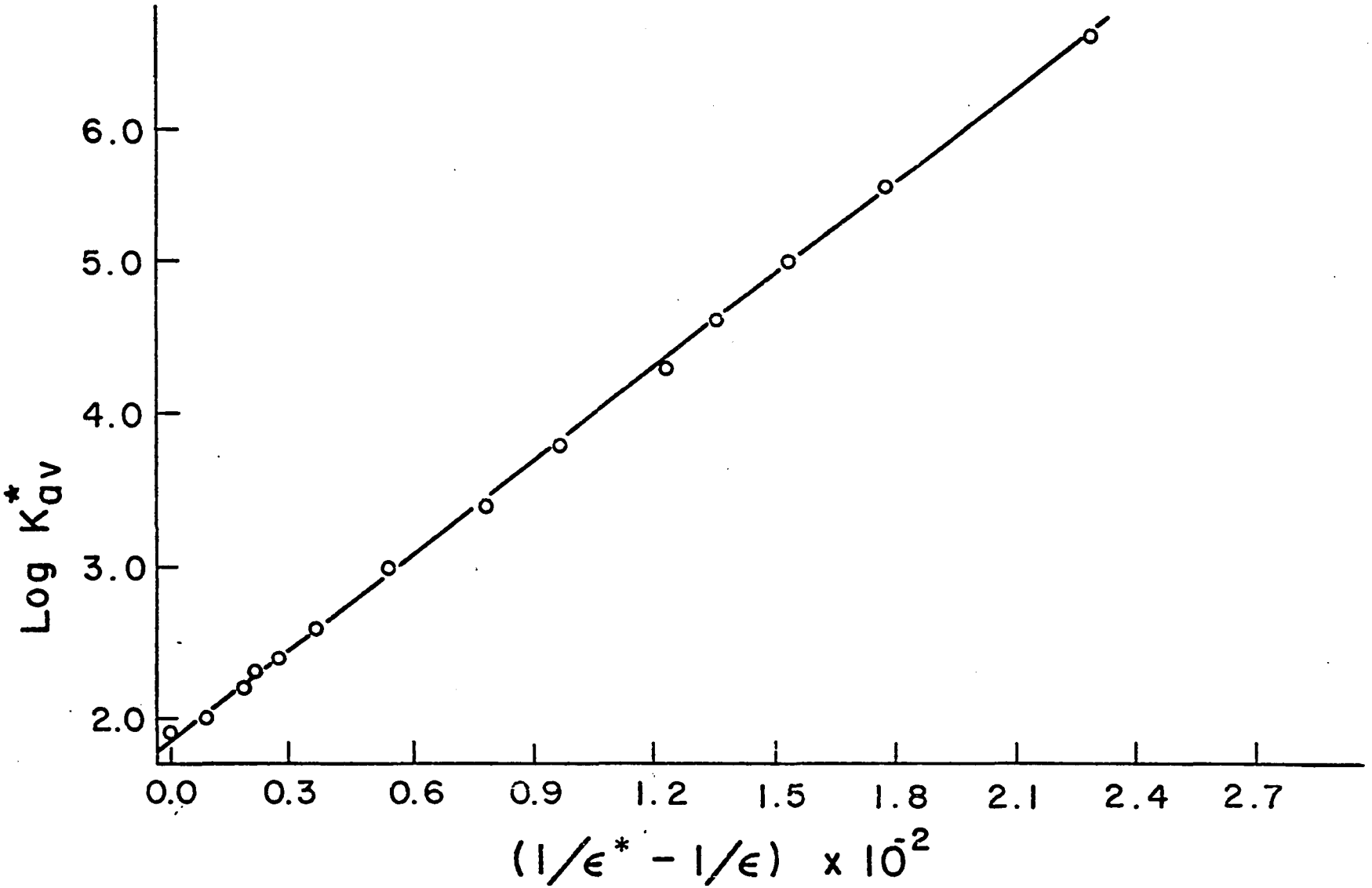

6.0
5.0
4.0
3.0
2.0
Log K^*_{av}
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
$(1/\epsilon^* - 1/\epsilon) \times 10^2$

FIGURE 11:

PLOT OF LOG K_{av}^{*} VERSUS $(1/\epsilon^{*} - 1/\epsilon)$ FOR ZINC (II) LACTATES IN ETHANOL-WATER MIXED SOLVENTS

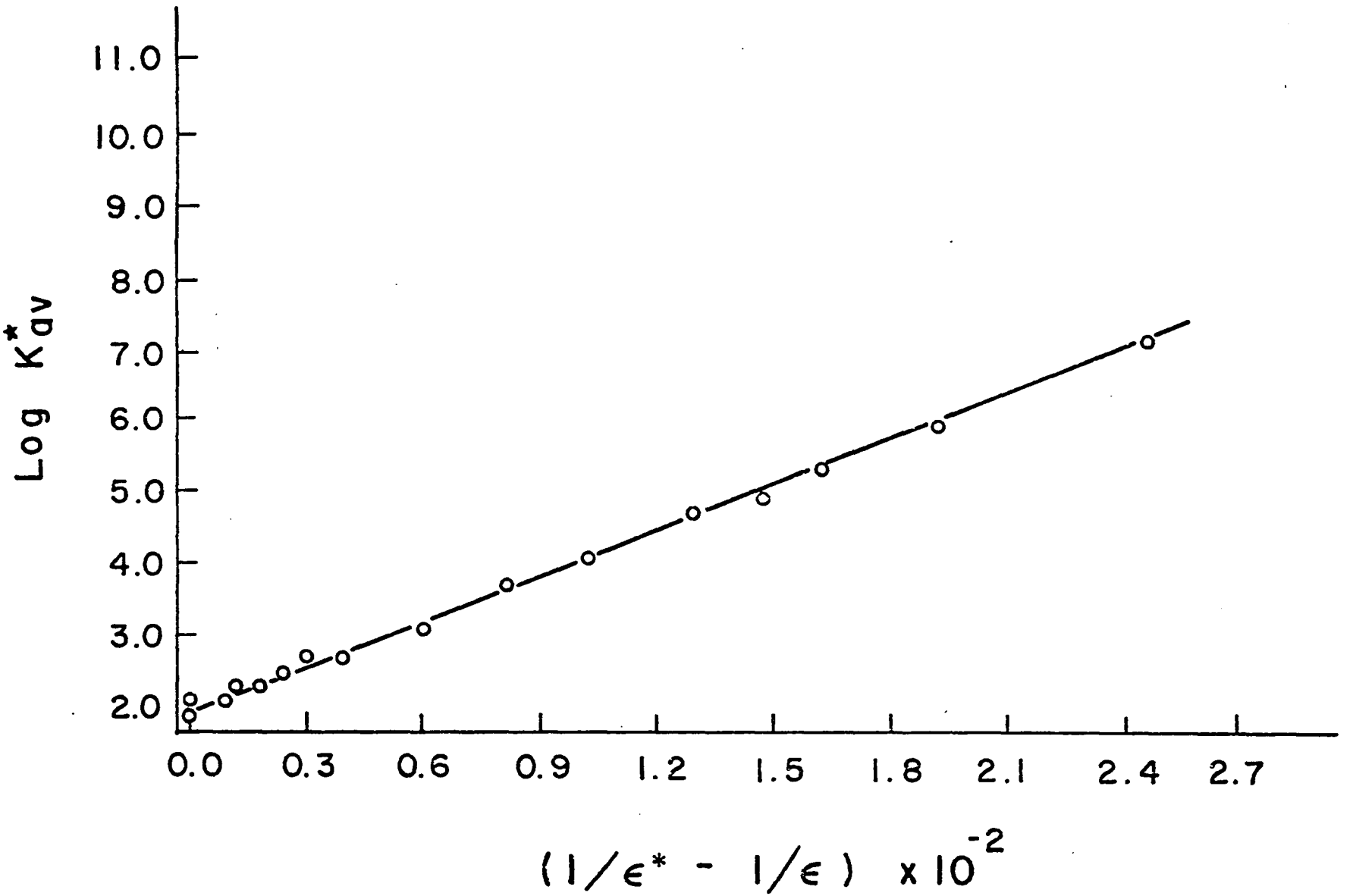
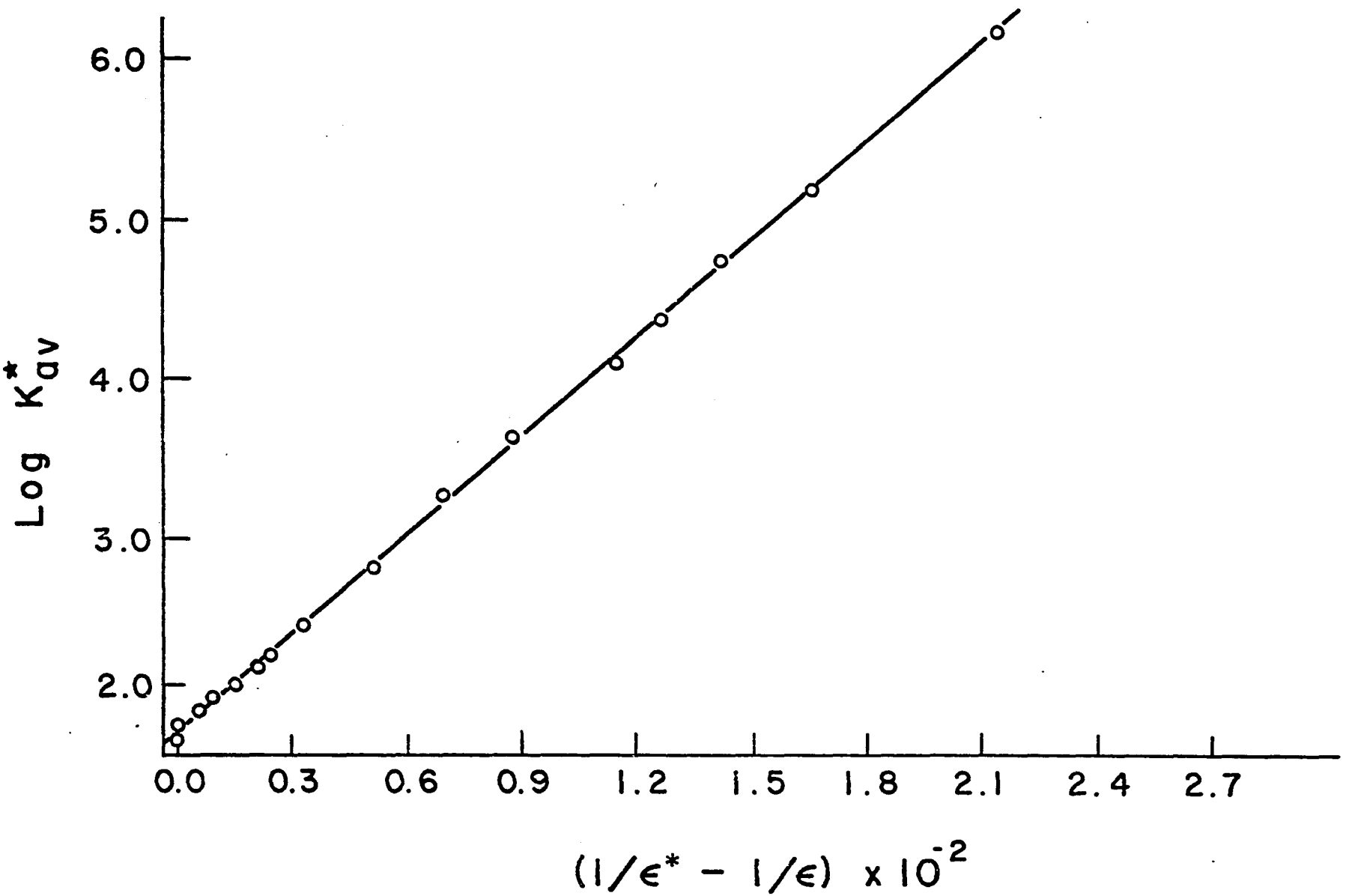

11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
Log K^*_{av}
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
$(1/\epsilon^* - 1/\epsilon) \times 10^{-2}$

FIGURE 12:

PLOT OF LOG K_{av}^{*} VERSUS $(1/\epsilon^{*} - 1/\epsilon)$ FOR ZINC (II) LACTATES IN GLUCOSE-WATER MIXED SOLVENTS


6.0
5.0
4.0
3.0
2.0
Log K^*_{av}
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
$(1/\epsilon^* - 1/\epsilon) \times 10^{-2}$

Since the plots are linear with the same intercept, and since the fundamental variable is the bulk dielectric constant, it is reasonable to assume that it should be possible to parameterize the plots in such a way as to represent all of them by one general equation. The appropriate variable turned out to be $(1/\epsilon^{*''} - 1/\epsilon'')$, in which

$$\epsilon^{*''} = \epsilon^{*} + (\epsilon - \epsilon_{org}) \tag{95}$$

and $$\epsilon'' = \epsilon + (\epsilon - \epsilon_{org}) = (2\epsilon - \epsilon_{org}) \tag{96}$$

Figure 13 is the plot of log K^{*}_{av} versus $(1/\epsilon^{*''} - 1/\epsilon'')$, and the equation of this graph is

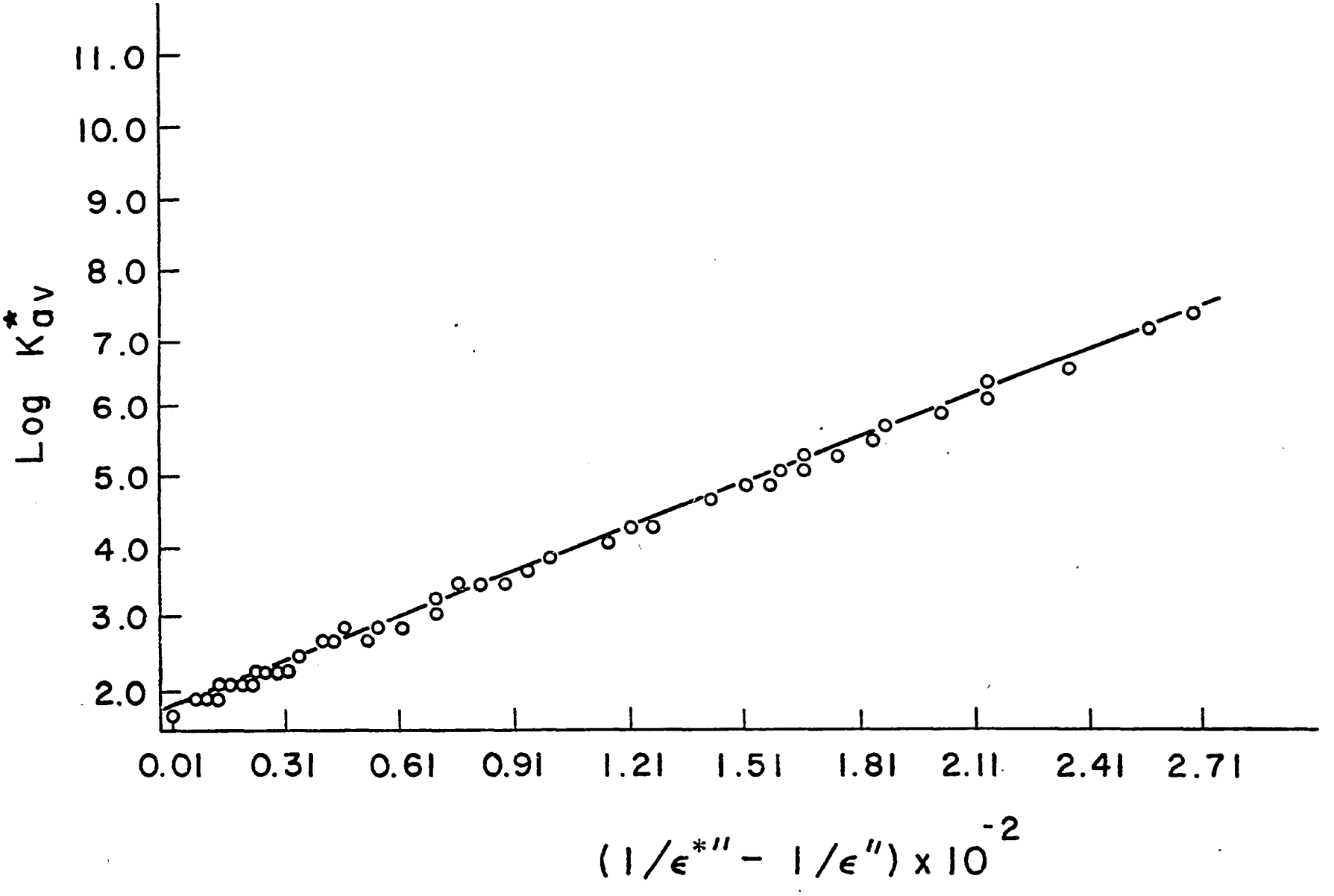
$$\log K^{*}_{av} = \log K_{av} + (1/\epsilon^{*''} - 1/\epsilon'') \tag{97}$$

which has the same general form as equation (87), derived from Born's electrostatic model for the formation of the complexes. According to equation (97), log K^{*}_{av} is a function of $(1/\epsilon^{*''} - 1/\epsilon'')$ only, regardless of the actual composition of the mixed solvent. Consequently, equation (97) is the function sought. In the region of very low dielectric constant, the plot curves upward, and an additional term, consisting of an exponential of base 10, is required for writing the appropriate analytical function of the graph in this region. This exponential is given by some linear combination, similar to the term multiplied by β in equation (97), of the reciprocals of the bulk dielectric constants of the solvents. Therefore, in the curved segment of the plot (that is, in solvents of low dielectric constant), the noncoulombic forces make significant contribution toward stabilizing the complex, and Born's electrostatic model is not adequate. For the linear portion of the graph (that is, in solvents of high dielectric constant), equation (97) is good; therefore, the coulombic forces predominate in stabilizing the complex, Born's model is valid, and the contribution of the noncoulombic forces toward stabilizing

FIGURE 13:

PLOT OF LOG K_{av}^{*} VERSUS $(1/\epsilon^{*''} - 1/\epsilon^{''})$ FOR

ZINC (II) LACTATES IN VARIOUS MIXED SOLVENTS


11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
Log K^*_{av}
0.01
0.31
0.61
0.91
1.21
1.51
1.81
2.11
2.41
2.71
$(1/\epsilon^{*\prime\prime} - 1/\epsilon'') \times 10^{-2}$

the complex is negligible.

Theories of ionic solutions are model theories and range from the more primitive models, in which mathematical treatments are possible, to very complex models, where only qualitative generalizations can be made. As more and more data are collected on systems involving ionic reactions in solution, it becomes increasingly apparent that the complexity of these systems makes an ab initio quantitative treatment less useful in the sense of predicting how different properties of the solvent will affect reactions involving ions. Most previous attempts to explain thermodynamic and kinetic data for metal ion complexation and formation reactions in solution in terms of singular properties of the solvent such as dielectric constant, basicity, dipole moment, etc., have had little success in the past. This is not unexpected, in that there are many factors involved in trying to evaluate the role of the solvent in complex ion formation reactions in solution. The structure of the solvent molecules around the ion, ligand and newly formed complex, as well as the nature of the ion-solvent interactions of these species in the bulk of the solvent, are all important factors. Although this study is of an exploratory nature and does not justify a detailed discussion of solvent effects on a molecular basis, nor does it involve itself with the determinations of these various intermediate solvated ions nor with their structures nor the structure of the final complex ion, nevertheless, it can be concluded as a result of our own studies that the formation constants of the metal complexes in various mixed solvent media can be related to each other through a function of their buld dielectric constants. In the absence of structural data, it is possible to discuss only in a qualitative way the implications and difference in the trends

of the formation constants of Ca (II) and Zn (ii) complexes on the one hand, and those of Fe (IlI) complexes on the other. We will make a very basic assumption here without direct experimental evidence. We propose that although the lactate anion is behaving as a bidentate ligand in these complexes, the two formation constants signal the attachment of two different lactate anions to the central metal ion, rather than the attachment of the first and second coordination sites of the same ligand to the central metal ion. In support of this assumption, we point out that both the formation constants are of nearly the same order of magnitude. Secondly, both attachments are observed at pH's considerably below the pH at which the enolic proton is likely to ionize. In fact, lactic acid exhibited only one ionization constant. However, after the attachment of the carboxylate anion to the metal, the enolic group is most conveniently located to coordinate with the metal. Such a coordination may not be too strong, due to the weak donor property of the enolic group; furthermore, there may be some steric strain if the size of the central metal ion is large, as in the cases of Ca^{2+} (0.99 A^{o}) and Zn^{2+} (0.74 A^{o}), making the coordination of the enolic group in fact endothermic. However such coordination will considerably increase the entropy of the system. Later in this section, we shall see that this is what precisely happens in the cases of the complexation of Ca (II) and Zn (Il).

Our basic assumption in empirically deriving a function from the experimental data has been that all three ions are spherical. Therefore, the first order coulombic interaction between the central metal ion and the ligands should be identical. Whereas this assumption is true for the pretransition Ca^{2+} (d^{0}) ion and the post-transition Zn^{2+} (d^{10}) ion, it may not be equally valid for the midtransition Fe^{3+} (d^{5}) ion. It

also follows from our basic assumption that the energies involved in the charging the central metal atom and the donor atoms, and the work involved in bringing these charged particles within the bonding proximity are the most important factors involved in stabilizing the complexes. As a first approximation, it would seem that the formation constants should follow the order of the ionization energies. This would give us the order K(Ca)>K(Fe)> K(Zn), instead of the experimentally observed sequence K(Fe) > K(Zn) > K(Ca). Emelius and Anderson (9) proposed that the most important factor involved in stabilizing an electrostatic bond (a limiting case) is the ionic potential, a term originally proposed by Fajans. Ionic potential is simply the ratio of the ionic charge to the ionic radius. It has frequently been observed with only a very few exceptions that when everything else is the same, an ion with a larger ionic potential forms a stabler complex. In fact, below a certain critical value of the ionic potential, the ions are not even hydrated. An inspection of Table XLV would suggest that the order of the formation constants should be K(Fe) > K(Zn) > K(Ca), as was indeed observed. In fact, it would seem on critical evaluation that the ionization energies of the gaseous atoms (Table XLIV) are rather poor criteria for rationalizing the order of the formation constants of the complexes.

Conceptually the process of charging and bringing the ions in close proximity for bond formation consists of a number of steps. These steps are (1) vaporization of the gaseous atom from the crystal; (2) excitation of the ground state gaseous atom, and hybridization of the orbitals to form a new set of equivalent valence orbitals; (3) promotion of the electrons to valence state orbitals; and (4) ionization from these valence state orbitals. Theoretically, the ligand species must also

TABLE XLIV

RADII, IONIZATION ENERGIES

AND ELECTRODE POTENTIALS OF Fe, Ca, and Zn (14)

	Fe	Ca	Zn
Atomic Number	26	20	30
Metallic radius Å	1.26	1.97	1.38
Ionic radius of M^{2+}(Å)	0.76	0.99	0.74
M^{3+}(Å)	0.67	--	--
Ionization energy I_1 (eV)	7.90	6.11	9.39
I_2 (eV)	16.16	11.87	17.89
E^o, M^{2+}/M (V)	-0.44	-2.87	-0.763
M^{3+}/M^{2+} (V)	+0.77	--	--

TABLE XLV

IONIC RADII AND IONIC POTENTIALS FOR SELECTED METAL CATIONS AS INDICATORS OF THEIR ORDERS OF RELATIVE REACTIVITY (9)

ION	IONIC RADIUS (Å)	IONIC POTENTIAL (Charge/Radius)
Cs^{+}	1.67	0.61
Rb^{+}	1.48	0.67
K^{+}	1.33	0.71
Na^{+}	0.98	1.0
Ba^{2+}	1.31	1.4
Hg^{2+}	1.12	1.8
Cd^{2+}	1.03	1.9
Ca^{2+}	0.98	1.9
Zn^{2+}	0.83	2.4
Co^{2+}	0.82	2.4
Ni^{2+}	0.78	2.5
Fe^{3+}	0.67	4.5
Co^{3+}	0.66	4.5
Cr^{3+}	0.65	4.6
Al^{3+}	0.57	5.3
Pt^{4+}	0.66	6.0
Be^{2+}	0.39	5.9

↑ Ions not hydrated generally no complex compounds formed ↓

Ions invariably hydrated ——→

Ions readily amminated - - - →

Ammines and innercomplex salts readily formed ——→

undergo a similar process. Finally, the bond formation between the valence state ions (atoms) must release enough energy to compensate for all of the inputs in order for the complex species to be stable. It turns out that the excitation-hybridization energy and the promotional energy play a critical role in complex stability. Generally, these two energy terms are small for the transition elements and large for pre- and post-transition elements. This again would suggest greater stability for the Fe (III) complexes.

We must also take into consideration the coordination number, the number of bonds and the probable geometry of the complex species. The existence of two successive formation constants of nearly the same order of magnitude strongly suggests coordination of two lactate anions via the carboxylate group. Presumably, the lactate anion behaves as a bidentate ligand through the use of its carboxylate and enolic groups, which will require the Ca (II) and Zn (II) valence orbitals to be tetrahedrally oriented. In fact, the pre- and post-transition metal complexes are most frequently tetrahedral through the use of the sp^3 hybrid valence orbital set.

Although we have been able to determine only two successive formation constants for the Fe (III) complex, we still suspect that the Fe (III) complex is hexacoordinated, the fifth and sixth positions being coordinated by the solvent molecules. The most common coordination polyhedron for Fe (III) complexes is the octahedron. In the reaction medium used in these studies, we believe that the octahedral geometry is the only possibility. However, this conclusion cannot be conclusively settled without the isolation of the complex and a study of its structure and electronic and vibrational spectra.

Again for a number of reasons, it is anticipated that the hexa-coordinated Fe (III) complex will be more stable than the tetraco-ordinated Ca (II) and Zn (II) complexes.

We should also try to rationalize the temperature dependence of the formation constants. The magnitude of the formation constants increases with increasing temperature for the Ca (II) and Zn (II) complexes, and it decreases with increasing temperature for the Fe (III) complex. Obviously, the trend for the Fe (III) complex is normal, whereas the trends for the Ca (II) and Zn (II) complexes are not normally expected. This would mean that complexation of Ca (II) and Zn (II) are perhaps entropy driven, as was mentioned earlier in this chapter. Entropy driven reactions are not unknown. A sample calculation is given below only to make the point more clear:

SAMPLE CALCULATIONS (16)

Zn(II) Lactate, 10% Methanol-Water Mixed Solvent, at a Temperature of 15°

$$\Delta H^{o} = \frac{T_2 \cdot T_1 \cdot R \cdot 2.303 \log K_2/K_1}{T_2 - T_1} = \frac{(313)(288)(1.987)(2.303)}{(25)} \log \frac{2.3\times10^{2}}{8.0\times10^{1}}$$

$\Delta H^{o} = +\ 7.60$ Kcal/mole

$\Delta G^{o} = -\ RT\ 2.303 \log K_{av}$ $\qquad \Delta G = (1.987)(288)(2.303) \log 8.0\times10^{1}$

$\Delta G^{o} = -\ 1.09$ Kcal/mole at 15°C

$$\Delta S^{o} = \frac{\Delta H^{o} - \Delta G^{o}}{T} = \frac{+\ 7.60 - (-\ 1.09)}{288} = 30.15 \text{ eu}$$

A great deal of confidence should not be placed on the actual numerical values of ΔH^{0} tabulated in Tables XLVI - LVII, since ΔH^{o} values are not too sensitive to the changes in the values of K_{av} with respect to temperature. The only conclusion that may be safely made is that the complexation of Ca (II) and Zn(II) by the lactate anion in the media investigated are endothermic, and hence must be entropy driven.

It should be noted that many endothermic, entropy driven processes in solution are known. It may only be speculated that the formation of calcium lactate in biological fluids may be one of the temperature balancing processes.

Obviously, there is less steric strain involved in the formation of the Fe (III) complexes due to the appropriate ionic radius (0.67 A^{o}), and as a result, the complexation process is both enthalpy and entropy driven.

The trends of K_1 and K_2 for the complexes of Ca (II) and Zn (II) are normal; that is, $K_1 > K_2$, although only to a small extent, the reason for which has already been explained. Sen (92) has shown that from statistical considerations only, K_1 should be greater than K_2. For the Fe (III) complexes, K_2 has been found to be greater than K_1 for the lactate complexes of Fe (III). Such a reversed order of the magnitude of formation constants is known for a number of other Fe (III) complexes, and it has been attributed to an enhanced entropy increase during the second step.

We are aware that in places our rationalization lacks direct experimental evidence, and in places it may seem somewhat stretched to the more discriminating reader. The next step of this particular research program must include isolation and structural characterization, which should provide more conclusive evidence.

It has recently come to our attention that Prout, et al., (83) have investigated and determined the structure of copper (II) lactate by x-ray crystallographic methods. Their findings show that the lactate anion behaves as a bidentate ligand, coordinating through the carboxylate group and the -OH group, without the loss of the -OH proton, as we had

TABLE XLVI: THERMODYNAMIC QUANTITIES OF ZINC COMPLEXES IN VARIOUS MIXED SOLVENTS AT 15°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	7.60	-1.09	30.15
20.00	0.123	8.09	-1.20	32.25
30.00	0.194	8.84	-1.32	35.26
50.00	0.360	10.74	-1.62	42.87
70.00	0.568	13.54	-2.06	54.17
80.00	0.692	14.87	-2.37	59.83
90.00	0.835	16.52	-2.73	66.79

ETHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	7.43	-1.12	29.68
20.00	0.089	8.09	-1.25	32.43
30.00	0.144	8.92	-1.42	35.87
50.00	0.281	11.40	-1.86	46.02
70.00	0.477	15.36	-2.52	62.06
80.00	0.610	19.00	-2.98	76.26
90.00	0.779	21.14	-3.56	85.74

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	7.14	-1.01	28.25
0.89	0.0009	7.17	-1.01	28.38
1.77	0.0018	7.18	-1.01	28.42

TABLE XLVII: THERMODYNAMIC QUANTITIES OF ZINC COMPLEXES IN VARIOUS MIXED SOLVENTS AT 25°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	5.47	-1.21	22.38
20.00	0.123	5.89	-1.32	24.18
30.00	0.194	6.73	-1.46	27.46
50.00	0.360	8.41	-1.79	34.21
70.00	0.568	11.35	-2.29	45.75
80.00	0.692	12.19	-2.63	49.71
90.00	0.835	13.45	-3.01	55.23

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	5.47	-1.24	22.47
20.00	0.089	6.31	-1.38	25.79
30.00	0.144	7.15	-1.56	29.21
50.00	0.281	9.67	-2.06	39.36
70.00	0.477	14.30	-2.80	57.33
80.00	0.610	16.40	-3.32	66.13
90.00	0.779	19.34	-3.95	78.13

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	5.13	-1.11	20.93
0.89	0.0009	5.13	-1.11	20.94
1.77	0.0018	5.17	-1.12	21.10

TABLE XLVIII: THERMODYNAMIC QUANTITIES OF ZINC COMPLEXES IN VARIOUS MIXED SOLVENTS AT 35°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	5.47	-1.33	22.04
20.00	0.123	5.89	-1.45	23.82
30.00	0.194	6.73	-1.61	27.05
50.00	0.360	8.41	-1.97	33.70
70.00	0.568	11.35	-2.53	45.06
80.00	0.692	12.19	-2.89	48.96
90.00	0.835	13.45	-3.31	54.40

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	5.47	-1.36	22.14
20.00	0.089	6.31	-1.52	25.40
30.00	0.144	7.15	-1.72	28.77
50.00	0.281	9.67	-2.27	38.76
70.00	0.477	14.30	-3.10	56.45
80.00	0.610	16.40	-3.67	65.12
90.00	0.779	19.34	-4.37	76.94

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	5.13	-1.22	20.62
0.89	0.0009	5.13	-1.23	20.63
1.77	0.0018	5.17	-1.23	20.78

TABLE XLIX: THERMODYNAMIC QUANTITIES OF ZINC COMPLEXES IN VARIOUS MIXED SOLVENTS AT 40°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	7.60	-1.47	28.96
20.00	0.123	8.09	-1.61	30.98
30.00	0.194	8.84	-1.77	33.87
50.00	0.360	10.74	-2.16	41.19
70.00	0.568	13.54	-2.75	52.04
80.00	0.692	14.87	-3.14	57.50
90.00	0.835	16.52	-3.59	64.20

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	7.43	-1.50	28.51
20.00	0.089	8.09	-1.66	31.16
30.00	0.144	8.92	-1.88	34.47
50.00	0.281	11.40	-2.45	44.23
70.00	0.477	15.36	-3.32	59.65
80.00	0.610	19.00	-3.95	73.28
90.00	0.779	21.14	-4.67	82.43

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	7.14	-1.36	27.14
0.89	0.0009	7.17	-1.37	27.25
1.77	0.0018	7.18	-1.37	27.30

TABLE L: THERMODYNAMIC QUANTITIES OF CALCIUM COMPLEXES IN VARIOUS MIXED SOLVENTS AT 15°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	8.18	-0.79	31.12
20.00	0.123	8.67	-0.90	33.21
30.00	0.194	9.33	-1.02	35.94
50.00	0.360	11.31	-1.32	43.84
70.00	0.568	14.12	-1.76	55.13
80.00	0.692	15.44	-2.07	60.79
90.00	0.835	17.10	-2.43	67.75

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	8.01	-0.82	30.64
20.00	0.089	8.67	-0.95	33.39
30.00	0.144	9.50	-1.12	36.83
50.00	0.281	11.98	-1.56	46.98
70.00	0.477	15.94	-2.22	63.02
80.00	0.610	19.57	-2.68	77.23
90.00	0.779	21.72	-3.26	86.70

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	7.71	-0.71	29.22
0.89	0.0009	7.75	-0.71	29.34
1.77	0.0018	7.75	-0.71	29.36

TABLE LI: THERMODYNAMIC QUANTITIES OF CALCIUM COMPLEXES IN VARIOUS MIXED SOLVENTS AT 25°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	7.15	-0.89	26.97
20.00	0.123	7.57	-1.01	28.78
30.00	0.194	8.41	-1.15	32.06
50.00	0.360	10.09	-1.48	38.81
70.00	0.568	13.03	-1.98	50.35
80.00	0.692	13.87	-2.32	54.30
90.00	0.835	15.14	-2.70	59.83

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	7.15	-0.92	27.07
20.00	0.089	7.99	-1.07	30.39
30.00	0.144	8.83	-1.25	33.81
50.00	0.281	11.35	-1.75	43.96
70.00	0.610	18.08	-2.49	61.93
80.00	0.610	18.08	-3.01	70.73
90.00	0.779	21.02	-3.64	82.73

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	6.81	-0.80	25.53
0.89	0.0009	6.81	-0.80	25.54
1.77	0.0018	6.85	-0.81	25.70

TABLE LII: THERMODYNAMIC QUANTITIES OF CALCIUM COMPLEXES IN VARIOUS MIXED SOLVENTS AT 35°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	7.15	-1.03	26.53
20.00	0.123	7.57	-1.16	28.31
30.00	0.194	8.41	-1.31	31.54
50.00	0.360	10.19	-1.68	38.19
70.00	0.658	13.03	-2.23	49.55
80.00	0.692	13.87	-2.60	53.45
90.00	0.835	15.14	-3.01	58.89

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	7.15	-1.06	26.63
20.00	0.089	7.99	-1.22	29.90
30.00	0.144	8.83	-1.42	33.26
50.00	0.281	11.35	-1.98	43.26
70.00	0.477	15.98	-2.80	60.95
80.00	0.610	18.08	-3.37	69.62
90.00	0.779	21.02	-4.07	81.43

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	6.81	-0.93	25.11
0.89	0.0009	6.81	-0.93	25.12
1.77	0.0018	6.85	-0.94	25.27

TABLE LIII: THERMODYNAMIC QUANTITIES OF CALCIUM COMPLEXES IN VARIOUS MIXED SOLVENTS AT 40°C.

METHANOL-WATER

WT% MeOH	XS MeOH	ΔH° K cal/mole	ΔG° K cal/mole	ΔS° Entropy Units
10.00	0.059	8.18	-1.17	29.83
20.00	0.123	8.67	-1.30	31.85
30.00	0.194	9.33	-1.47	34.48
50.00	0.360	11.31	-1.86	42.06
70.00	0.568	14.12	-2.45	52.92
80.00	0.692	15.44	-2.83	58.37
90.00	0.835	17.10	-3.28	65.07

ETHANOL-WATER

WT% EtOH	XS EtOH	ΔH° K cal/mole	ΔG° K cal/mole	ΔS° Entropy Units
10.00	0.042	8.01	-1.19	29.39
20.00	0.089	8.67	-1.36	32.03
30.00	0.144	9.58	-1.57	35.35
50.00	0.281	11.98	-2.15	45.11
70.00	0.477	15.94	-3.01	60.53
80.00	0.610	19.57	-3.65	74.16
90.00	0.779	21.72	-4.37	83.30

GLUCOSE-WATER

WT% Glucose	XS Glucose	ΔH° K cal/mole	ΔG° K cal/mole	ΔS° Entropy Units
0.18	0.0002	7.71	-1.06	28.01
0.89	0.0009	7.75	-1.06	28.13
1.77	0.0018	7.75	-1.07	28.14

TABLE LIV: THERMODYNAMIC QUANTITIES OF IRON COMPLEXES IN VARIOUS MIXED SOLVENTS AT 15°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	-6.61	-2.33	-14.84
20.00	0.123	-6.11	-2.44	-12.74
30.00	0.194	-5.29	-2.56	- 9.46
50.00	0.360	-3.47	-2.86	- 2.12
70.00	0.568	-0.66	-3.30	9.17
80.00	0.692	0.66	-3.61	14.83
90.00	0.835	2.31	-3.97	21.79

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	-6.77	-2.36	-15.32
20.00	0.089	-6.11	-2.49	-12.57
30.00	0.144	-5.29	-2.66	- 9.12
50.00	0.281	-2.81	-3.10	1.02
70.00	0.477	1.16	-3.76	17.07
80.00	0.610	4.79	-4.22	31.27
90.00	0.779	6.94	-4.80	40.75

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	-7.07	-2.25	-16.74
0.89	0.0009	-7.04	-2.25	-16.62
1.77	0.0018	-7.04	-2.25	-16.60

TABLE LV: THERMODYNAMIC QUANTITIES OF IRON COMPLEXES IN VARIOUS MIXED SOLVENTS AT 25°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	-4.62	-2.30	-7.78
20.00	0.123	-4.20	-2.42	-5.97
30.00	0.194	-3.36	-2.56	-2.70
50.00	0.360	-1.68	-2.89	4.06
70.00	0.568	1.26	-3.39	15.60
80.00	0.692	2.10	-3.73	19.55
90.00	0.835	3.36	-4.11	25.07

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	-4.62	-2.33	-7.68
20.00	0.089	-3.78	-2.48	-4.37
30.00	0.144	-2.04	-2.66	-0.95
50.00	0.281	-0.42	-3.16	9.20
70.00	0.477	4.20	-3.90	27.18
80.00	0.610	6.31	-4.42	35.98
90.00	0.779	9.25	-5.05	47.97

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	-4.96	-2.21	-9.23
0.89	0.0009	-4.96	-2.21	-9.21
1.77	0.0018	-4.92	-2.22	-9.06

TABLE LVI: THERMODYNAMIC QUANTITIES OF IRON COMPLEXES IN VARIOUS MIXED SOLVENTS AT 35°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	-4.62	-2.31	-7.50
20.00	0.123	-4.20	-2.44	-5.72
30.00	0.194	-3.36	-2.60	-2.40
50.00	0.360	-1.68	-2.96	4.16
70.00	0.568	1.26	-3.52	15.52
80.00	0.692	2.10	-3.88	19.42
90.00	0.835	3.36	-4.30	24.86

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	-4.62	-2.35	-7.40
20.00	0.089	-3.78	-2.51	-4.13
30.00	0.144	-2.94	-2.71	-0.77
50.00	0.281	-0.43	-3.26	9.23
70.00	0.477	4.20	-4.00	26.92
80.00	0.610	6.31	-4.66	35.59
90.00	0.779	9.25	-5.36	47.40

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	-4.96	-2.21	-8.92
0.89	0.0009	-4.96	-2.22	-8.91
1.77	0.0018	-4.92	-2.22	-8.76

TABLE LVII: THERMODYNAMIC QUANTITIES OF IRON COMPLEXES IN VARIOUS MIXED SOLVENTS AT 40°C

METHANOL-WATER

WT% MeOH	XS MeOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.059	-6.61	-2.28	-13.81
20.00	0.123	-6.11	-2.42	-11.70
30.00	0.194	-5.29	-2.58	- 8.63
50.00	0.360	-3.47	-2.97	- 1.85
70.00	0.568	-0.66	-3.57	9.28
80.00	0.692	0.66	-3.95	14.73
90.00	0.835	2.31	-4.40	21.43

ETHANOL-WATER

WT% EtOH	XS EtOH	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
10.00	0.042	-6.77	-2.31	-14.25
20.00	0.089	-6.11	-2.48	-11.61
30.00	0.144	-5.29	-2.69	- 8.29
50.00	0.281	-2.81	-3.27	16.89
70.00	0.477	1.16	-4.13	16.89
80.00	0.610	4.79	-4.77	30.52
90.00	0.779	6.94	-5.48	39.66

GLUCOSE-WATER

WT% Glucose	XS Glucose	H^o Kcal/mole	G^o Kcal/mole	S^o Entropy Units
0.18	0.0002	-7.07	-2.17	-15.63
0.89	0.0009	-7.04	-2.18	-15.51
1.77	0.0018	-7.04	-2.18	-15.50

assumed from the absence of a second ionization constant of lactic acid and from the formation of the complexes at relatively low pH's. This fact would also support our premise that the two-stage formation of the metal complex proceeds through nearly identical mechanisms of attachment of the two carboxylate groups (as we had supposed from our nearly equal K_1's and K_2's).

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VITA

James Joseph Gibbons was born in Springfield, Missouri, on October 31, 1946. After attending the Springfield public schools, he enrolled in Drury College where he received the A.B. degree cum laude in Chemistry and Mathematics, with Departmental Distinction in Chemistry, in 1968. After working for a year and a half as a research chemist with the Hoffman-Taff Division of Syntex Pharmaceuticals, Inc., Mr. Gibbons was commissioned in the Army Medical Service Corps by direct appointment of the President at Fort Sam Houston, San Antonio, Texas. Upon completion of his military service, he assisted Dr. Rabindra N. Roy, LSU 1966, Professor and Chairman of the Department of Chemistry, Drury College, in a research program which culminated in the publication of eight papers co-authored by Mr. Gibbons.

In 1971, he entered the Louisiana State University upon receiving a Graduate Teaching Assistantship from the Department of Chemistry, and is presently a candidate for the degree of Doctor of Philosophy with a major in Inorganic Chemistry and a minor in Analytical Chemistry.

Mr. Gibbons is a member of the American Chemical Society, the American Association for the Advancement of Science, Phi Eta Sigma, Omicron Delta Kappa, Alpha Chi Sigma, Phi Lambda Upsilon, Sigma Pi Sigma, and Sigma Xi. In addition, he is an Associate Member of the American Association of University Professors and the Missouri Academy of Science.

EXAMINATION AND THESIS REPORT

Candidate: James Joseph Gibbons

Major Field: Chemistry

Title of Thesis: Effect of Medium on the Formation Constants Metal Complexes of Lactic Acid

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

December 18, 1974